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The Maumee River Basin Pilot Watershed Study Volume II. Sediment, Phosphates, and Heavy Metal Transport, Defiance Area, Ohio

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Maumee River Pilot Watershed Study

Sediment, Phosphates, and Heavy Metal Transport

Defiance Area, Ohio

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The United States Environmental Protection Agency was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment.

The Great Lakes National Program Office (GLNPO) of the U.S. EPA, was established in Region V, Chicago to provide a specific focus on the water quality concerns of the Great Lakes. GLNPO provides funding and personnel support to the International Joint Commission activities under the US-Canada Great Lakes Water Quality Agreement.

Several land use water quality studies have been funded to support the Pollution from Land Use Activities Reference Group (PLUARG) under the Agreement to address specific objectives related to land use pollution to the Great Lakes. This report describes some of the work supported by this Office to carry out PLUARG study objectives.

We hope that the information and data contained herein will help planners and managers of pollution control agencies make better decisions for carrying forward their pollution control responsibilities.

Dr. Edith J. Tebo
Director
Great Lakes National Program Office

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16. ABSTRACT Losses of nutrients and sediment from agricultural land were monitored during 1975-1977 in the Maumee River Basin, Ohio. These results have been reported in Volume 1, Watershed Characteristics and Pollutant Loadings. Special studies were made on sediment mineralogy and chemistry and on sediment, pesticide, and metal sediment transport.

Suspended sediments were higher in total-P (phosphorus) and labile-P than soils or stream-bottom sediments. Sediments are enriched in P during erosion and transport because of preferential transport of clay which is higher total P than the whole soil. Some P enrichment of suspended sediment was due to concentration by algae in the stream. Photo-synthetic consumption of carbon dioxide by algae caused formation of secondary calcite.

Preferential clay transport changed sediment mineralogy from its original soil mineralogy. No significant mineral alteration during sediment transport was found. Aggregated clay was found in runoff sediment as well as in stream-bottom sediment.

Heavy metal concentrations were low and indicated that groundwater and eroded soil were the major source. A point-source chrominum discharge was absorbed by stream sediment and taken up by rooted macrophytes. Pesticide scan of soils and bottom sediments showed only traces of DDT and other persistent chlorinated hydrocarbons. No other pesticides were detacted in significant quantities.

The watershed characteristics and pollutant loadings are discussed in Volume 1.

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Volume II
Sediment, Phosphates, and Heavy Metal Transport

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ABSTRACT

Losses of nutrients and sediment from agricultural land were monitored during 1975-1977 in the Maumee River Basin of Ohio. These results have been reported in Volume 1 of the report, Watershed Characteristics and Pollutant Loadings. A number of special studies on the mineralogy, chemistry, and transport of sediment, as well as pesticide and metal sediment transport, were conducted as part of the project. They are reported here as separate sections.

Maumee River Basin suspended sediments were found to be higher in total-P and labile-P than soils or stream-bottom sediments. Sediments are enriched in P during erosion and transport as a consequence of preferential transport of clay, which is higher in total-P than the whole soil. Some P enrichment of suspended sediment was due to concentration by algae in the stream. Photosynthetic consumption of CO_2 by algae was responsible for formation of secondary calcite in the stream.

Changes in sediment mineralogy from its original soil mineralogy was a result of preferential clay transport. There was no evidence of significant mineral alteration during sediment transport.

The Maumee River environment was found to be conducive to coagulation of fine and coarse clay soil and sediment into larger aggregates. Aggregated clay was found in runoff sediment as well as in stream-bottom sediments.

Heavy metals in Maumee River Basin water and sediment were determined. Levels were low and indicated that groundwater and eroded soil were the major source. Although a number of point sources were identified throughout the Basin, they had little effect on loadings to Lake Erie. A point-source chromium discharge was absorbed by stream sediment and taken up by rooted macrophytes.

Pesticide scan of Maumee River Basin soils and bottom sediments showed only traces of DDT and other persistent chlorinated hydrocarbons. No other known pesticides in the scan were detected in significant quantities.

The watershed characteristics and pollutant loadings are discussed in Volume 1 of this report.

1. SUMMARY

Special studies conducted in conjunction with watershed monitoring focused on the characteristics of stream sediment: their susceptibility to fluvial transport, changes in the characteristics of the original soil material during its passage through the stream system, and the chemical reactivity of sediment in the adsorption/desorption of nutrients and other chemicals.

These studies showed that the Maumee River Basin sediments are fine-textured, chemically reactive, and high in nutrients. This is due to the high clay content of the native soils and their relatively youthful nature.

Total-P content of Basin soils are high ($\sim$700 ug P/g sediment) and even higher in sediments ($>$ 1000 ug/g). This is a result of the higher clay content of sediment and the enrichment of phosphorus in the clay fraction of mineral soils. Basin soils and sediments have a large capacity to adsorb P, especially stream-bottom sediments, while suspended sediments were high in labile or P that could be desorbed into solution. Basin sediments, therefore, have the capacity to reduce high point-source concentrations of soluble P entering the stream and yet can release large amounts of P to algae or other aquatic vegetation.

Runoff and stream sediments were shown to be flocculated, i.e. clay-sized, particles that had coagulated into silt and sand-sized floccules. High Ca^{2+} status of Maumee Basin streams is responsible for coagulation of negatively charged clay particles.

Decomposition of soil minerals or formation of secondary minerals during sediment transport was studied. Mineralogy of stream sediment was found to be somewhat different from that of the original soil. Sediments were higher in illite and expandable minerals and lower in vermiculite than soils, but this difference was attributed to preferential clay transport rather than to mineral alteration. Secondary calcite was formed in suspended sediment during summer months. High algal activity resulted in CO_2 consumption and shift of the carbonate equilibrium toward calcite formation. In the anaerobic bottom-sediment environment, there appeared to be some changes in the iron oxide mineralogy.

Heavy metals were measured in Basin soils, sediments, and waters. Metal levels were at background levels in all cases, and groundwater appears to be a major source of metal loadings for the Basin. Point sources of metals were scattered throughout the Basin, and, although they contribute little to the total Basin metal load, their effect on near-downstream water quality can be severe. A chromium discharge into the Ottawa River at Lima, Ohio increased metal content of bottom sediments and rooted macrophytes.

Pesticide scan of Basin agricultural soils and stream-bottom sediments revealed only traces of persistent chlorinated hydrocarbons such as DDT and dieldrin.

2. INTRODUCTION

The special studies reported here in Volume 2 of the Maumee River Basin Pilot Watershed Study final report were conducted separately and constituted in most cases M.S. or Ph.D. thesis research. They are accordingly treated here as separate chapters, each representing a complete report of that work.

For a more complete description of the Maumee River Basin, its physical characteristics, land use,and pollutant loadings, the reader should consult Volume 1 of this report. Most of the special studies were conducted on the small agricultural watersheds monitored during this study as well as other sites in the Basin. These are identified in Figure 1 and Table 1. More specific site data are provided in the individual reports.

Figure 1. Sampling sites in the Maumee Basin

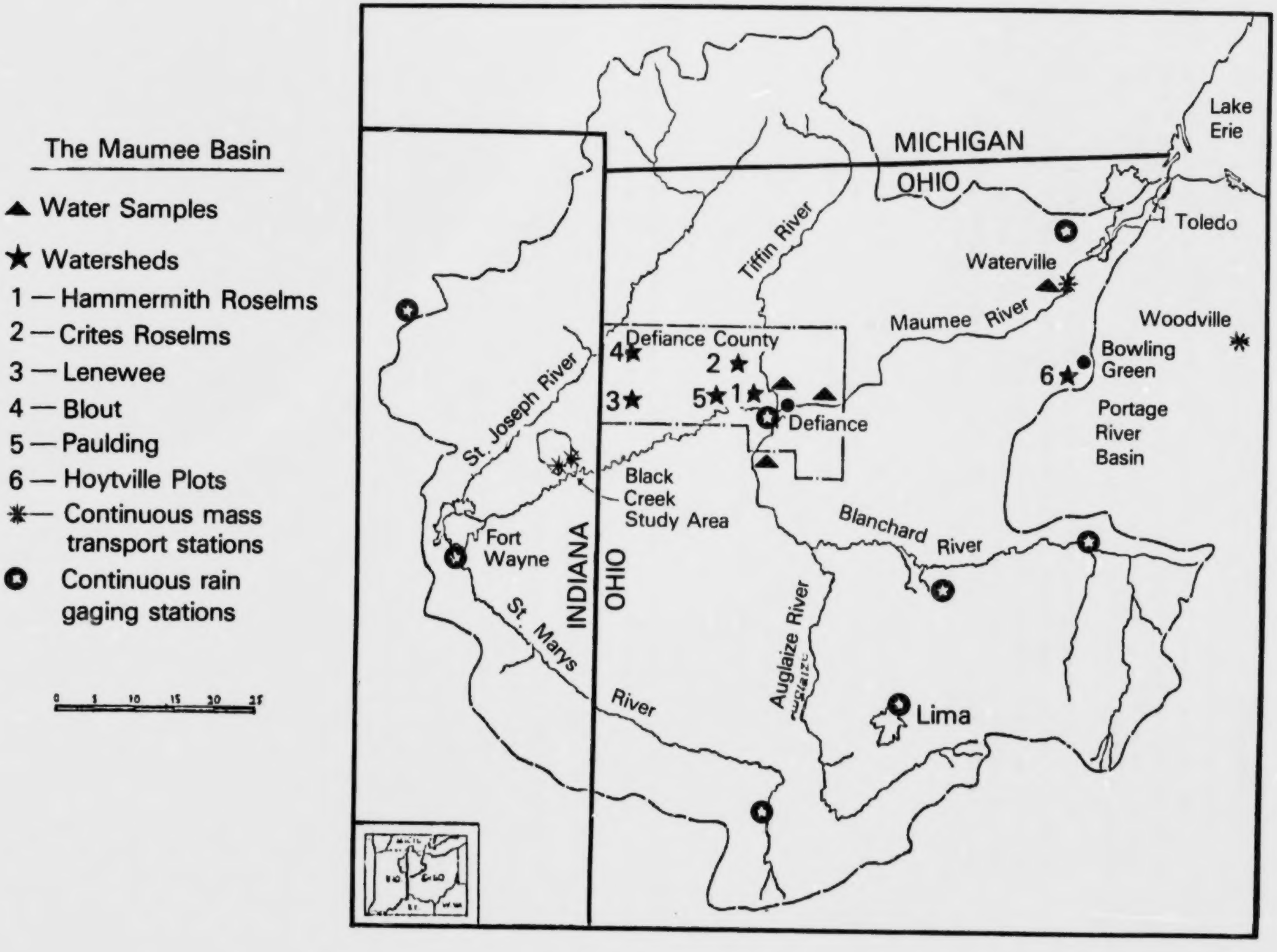
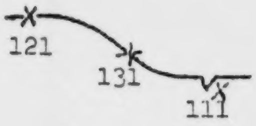

The Maumee Basin
▲ Water Samples
★ Watersheds
1 — Hammermith Roselms
2 — Crites Roselms
3 — Lenewee
4 — Blout
5 — Paulding
6 — Hoytville Plots
✳— Continuous mass transport stations
● Continuous rain gaging stations
0 5 10 15 20 25
MICHIGAN
OHIO
INDIANA
Lake Erie
Toledo
Waterville
Maumee River
Woodville
Bowling Green
Portage River Basin
Tiffin River
Defiance County
Defiance
St. Joseph River
Black Creek Study Area
Fort Wayne
St. Marys River
Blanchard River
Auglaize River
Lima

Table 1. Summary of watershed sites and plots

CODE	DOMINANT SOIL	PHYSIOGRAPHIC REGION	GEOLOGIC MATERIALS	SLOPE (%)	HECTARES	DRAINAGE SYSTEM	REMARKS
			DEFIANCE COUNTY				
111	Roselms	Lake Plain	Lake Clays	3-15	3.2	Surface	Complex Slopes
201	Roselms			3-5	0.6	Surface	
301 & 302	Lenawee			< 1	0.8 0.1	Surface & Tile	
501 & 502	Paulding			1	1.0	Surface & Tile	
401 & 402	Blount	Till Plain	Clay Loam Till	3-4	0.9	Surface & Tile	Dissected Uplands
			WOOD COUNTY				
611 to 682	Hoytville	Lake Plain	Clay Till	< 1	0.04	Surface & Tile	OARDC Drainage Plots

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3. RESULTS

3.1 Phosphate adsorption-desorption characteristics of soils and bottom sediments in the Maumee River Basin of Ohio

3.11 Abstract

Langmuir adsorption isotherms showed that Maumee River Basin sediments had adsorption capacities 10 to 20 times greater than Basin soils. Although the soil-clay fractions had adsorption capacities higher than the whole soil, they were considerably less than those of the sediments, and the difference is attributed to the higher content of amorphous or low-range order Fe and Al components in the bottom sediments. Equilibrium phosphorus concentration (EPC) and P desorbed was similar for soils and sediments as well as total P, indicating that although the bottom sediments have a high capacity to adsorb P, this capacity has not been realized. Correlations between adsorption-desorption parameters and soil/sediment properties are presented. Bray P1 "available" P was highly correlated with EPC and P desorbed in the soils but to a lesser extent in the bottom sediments. CDB and oxalate extractable-Fe was highly correlated with P adsorption capacity in the bottom sediments but not in the soils.

3.12 Introduction

In recent years, increased attention has been focused on the problem of additions of phosphates to natural waters, particularly as evidenced in accelerated eutrophication of lakes. Soluble phosphorus, as opposed to nitrogen, is often singled out as the factor limiting the growth of excess biomass in a body of water,due to the relatively small inputs of phosphorus compared to nitrogen, as well as the difficulty in controlling the many forms of N (1,11). Although urban and industrial wastes are major sources of phosphates to the Great Lakes, runoff from urban and agricultural land is assuming major importance as other sources diminish or are removed entirely (1,2,3). Non-point source losses of P in eroded material from the soil surface are diffuse and widespread and as such are difficult to quantify and control. Similarly, tile drainage and groundwater, which are often overlooked in typical phosphorus movement studies, can add significant quantities of P to streams and lakes (3,13).

The dissolved-particulate phosphorus balance of a stream or lake is controlled largely by the adsorption-desorption reactions with sediments carried by the water. The mechanism in aquatic systems appears to be based on specific anion adsorption such as described by Hingston et al (9,10), rather than mechanisms proposed solely for soils where localized P concentrations may be quite high and pH's low. Adsorption is most strongly associated with amorphous or,at most,short-range ordered secondary hydroxy iron coatings (22,26,27). Soluble phosphate may be adsorbed and transported or desorbed into solution, depending on ambient pH, solution phosphorus status, presence of competing anions, and redox potential (5,14,15,25).

The first objective of this study was to determine the phosphate sorption properties of a group of typical agricultural soils and compare them with stream-bottom sediments presumed to be eroded from similar soils. Secondly, the sorption properties were related to selected chemical and physical properties of the soils and sediments to determine the principal factors associated with sorption by the two types of adsorbents.

3.13 Methods and materials

Samples of five Ap horizons from soils of agricultural watersheds in Defiance County, Ohio, and one additional soil from the Northwest Branch, Ohio Agricultural Research and Development Center (OARDC), were collected for a study of phosphorus sorption. They represent some of the major agricultural soils of the Maumee River Basin of northwestern Ohio and have been developed from glacial lacustrine clays or clayey till. The soils chosen for study were Roselms silty clay (Aeric Ochraqualf, very fine, illitic, mesic); Broughton silty clay (Aeric Hapludalf, very fine, illitic, mesic); Lenawee silty clay loam (Mollic Haplaquept, fine illitic, nonacid, mesic); Paulding silty clay (Typic Haplaquept, very fine, illitic, nonacid, mesic); Blount loam (Aeric Ochraqualf, fine, illitic, mesic); and Hoytville clay loam (Mollic Ochraqualf, fine illitic, mesic). The soil samples were air-dried, ground, and the less than 2mm portion retained.

Five stream-bottom sediment samples (0-10cm depth) were also collected for comparison of their phosphate sorption behavior to that of the surface soils. The sediments were stored as a slurry in tightly sealed polyethylene containers at 4°C. Portions of the sediments were wet-seived and the less than 2mm fraction retained, also as a slurry at 4°C. The bottom sediments are primarily of surface soil origin, since stream-bank erosion in the Maumee River Basin is $<$10% of the total sediment load.

The soil samples and bottom sediments, plus the total clay ($<$ 2 u) fractions of the soils, were analyzed for a series of chemical and physical properties. Particle-size distribution was determined by pipet with sodium hexametaphosphate dispersion; pH with a 10:1 suspension: soil ratio in 0.01$\underline{M}$ $CaCl_2$; organic carbon by incineration[1]; inorganic (carbonate) carbon by gas evolution (4); total P by perchloric acid digestion (23); inorganic P by NaOH/HCl extraction (17); organic P by difference between the total and inorganic fractions; and "available" P by Bray P1 extraction (2). The results of these analyses are shown in Table 1. The soils, sediments, and clays were also characterized for various iron, aluminum, and silica fractions, including "amorphous" Fe and Al (21); "free oxides" of Fe and Al (16); and amorphous silica (8). These data are given in Table 2.

The phosphate-sorption characteristics determined for the soils, sediments, and clays (obtained by sedimentation after ultrasonic dispersion) included adsorption maximum and adsorption energy parameter, using the Langmuir isotherm (18), equilibrium phosphorus concentration (EPC) (25), and sequentially desorbed phosphorus.

Five-gram samples of soil or bottom sediment, or 2.5 grams of clay, the latter two as a slurry, were equilibrated with a graded series of phosphate solutions (as KH_2PO_4) in polyethylene tubes for 24 hr on a rotary shaker. Five drops of toluene were added to retard microbial growth, and the tubes were made to volume such that their final concentration was 0.01$\underline{M}$ with respect to $CaCl_2$. At the end of 24 hr, the tubes were centrifuged until clear and the supernatant filtered through a 0.2um filter membrane. An aliquot of the filtrate was analyzed for soluble inorganic P by the method of John (12). P adsorbed or desorbed per unit mass of adsorbent was calculated and plotted in the single-phase Langmuir isotherm form as $c/(x/m)$ vs c, where c is final solution concentration and x/m is the quantity of P adsorbed per unit mass of adsorbent, according to the general equation:

$$c/(x/m) = c/b + 1/kb \qquad (17)$$

The constants k and b can be found from the slope and intercept of the resulting curve where b is the P adsorption maximum and k is a parameter related to the energy of adsorption.

---

[1] Post, G. J. 1958. A study of three methods for determination of organic carbon in Ohio Soils of several great groups and the profile distribution of carbon-nitrogen ratios. M.Sc. thesis. The Ohio State University.

EPC, i.e. that solution concentration in which phosphorus is neither adsorbed nor desorbed, was determined from a plot of c vs x/m, where all units are as defined previously. Sequentially desorbed phosphorus was determined by summing the total P desorbed per unit mass of soil or sediment after ten successive 6-hour desorptions into 0.01M $CaCl_2$ at a 10:1 suspension: soil ratio.

Simple product-moment correlations were calculated among all sorption variables (adsorption maximum, adsorption energy parameter, EPC, and sequentially desorbed P) with the chemical and physical properties determined by the various adsorbents. Correlations were also calculated among all sorption variables themselves.

Phosphorus-Enrichment in Surface Runoff

Total sediment phosphorus content of runoff from the agricultural watersheds in Defiance County and Hoytville plots (Table 1, page 5) was determined by subtracting filtered reactive-P from total-P and dividing by sediment concentration. This calculation overestimates total sediment-P, because the total-P determination includes dissolved organic-P, which we did not measure. However, at sediment concentrations $>$ 100 ug/ml, this error is negligible. Therefore, only samples with sediment concentrations $>$ 100 ug/ml were used.

In addition, on a few selected samples, percent clay in the soil and runoff were determined as well as total-P in soil, soil-clay fraction and runoff as described previously. A clay-enrichment ratio was calculated as percent clay in runoff divided by percent clay in surface soil. Phosphorus-enrichment ratio was calculated in the same manner.

3.14 Results and Discussion

Adsorbent Characteristics

Particle-size distribution of the surface soils in the study (Table 1) strongly shows the influence of parent material. The soils range from a low of 22% clay (Blount) to a high of 47% clay (Paulding), with the difference largely made up in the sand separate. The clays of the surface soils are principally in the coarse (0.2-2um)-size fraction. There is, on the other hand, a much wider particle-size variation in the stream-bottom sediments examined. Of special note is the Independence 12-1-75 sample, which is very sandy (88%) and atypical of Maumee Basin sediments as a whole. It was collected under high-flow conditions relatively close to the stream bank and may represent unmixed stream bank scour material.

Phosphorus status of the soils, clays, and sediments varies widely (Table 1). Total P values show broad ranges for the surface soils, from 450 to 1018 ug P/g soil for the Blount and Roselms whole soils, respectively, while the clay fractions of the soils show similar trends over a somewhat narrower range. Inorganic P levels are lower and more tightly grouped for both soils and clays.

Table 1. Some physical and chemical properties of the soils, their clay fractions and bottom sediments.

	Sand	Silt	Fine clay	Coarse clay	Total clay	Total-P	Inorganic P	Available-P	Organic-C	$CaCO_3$ equivalent	pH
	%					ug/g			%		
Soils											
Roselms I	7.0	46.0	12.5	34.5	47.0	1018	704	26.8	1.82	0	6.4
Broughton	6.6	45.1	10.8	37.5	48.3	568	310	2.7	1.74	0	7.3
Roselms II	10.4	46.8	10.9	31.9	42.8	554	333	15.8	1.76	0	6.0
Lenawee	12.4	53.7	9.5	24.4	33.9	976	662	46.4	2.13	0	6.6
Blount	35.4	42.6	4.5	17.5	22.0	450	248	13.7	1.47	0	5.4
Paulding	5.1	49.5	9.7	35.7	45.4	780	421	8.6	2.37	0	6.7
Hoytville	18.7	42.4	11.1	27.8	38.9	816	566	21.7	2.24	0	7.1
Soil clay fractions											
Roselms I						889	636	nd*	1.66	0	nd
Broughton						705	438	nd	1.30	0	nd
Roselms II						738	420	nd	1.54	0	nd
Lenawee						1290	849	nd	2.78	0	nd
Blount						998	579	nd	2.56	0	nd
Paulding						904	437	nd	2.01	0	nd
Hoytville						1120	650	nd	2.22	0	nd
Bottom Sediments											
Ind. 12-1-75	88.9	6.0	1.1	4.0	5.1	476	379	36.7	0.95	12.8	7.3
Aug. 12-1-75	1.7	57.9	6.5	33.9	40.4	1260	1064	28.6	2.07	6.6	6.9
Tiffin 12-1-75	45.5	31.3	5.0	18.2	23.2	753	642	24.2	2.04	8.1	7.0

Table 1. continued

	Sand	Silt	Fine clay	Coarse clay	Total clay	Total-P	Inorganic-P	Available-P	Organic-C	$CaCO_3$ equivalent	pH
	%					ug/g			%		
Bottom Sediments											
Ind. 3-24-76	24.4	37.6	6.8	31.2	38.0	949	692	19.0	1.91	9.9	7.0
Aug. 3-24-76	3.4	47.5	8.8	40.3	49.1	1150	965	13.9	1.82	6.4	6.9

* Available P and pH not determined for clay fractions.

Available P in the surface soil varies from quite low at 2.7 ug/g (Broughton) to moderately high at 46.4 ug/g (Lenawee).

Citrate-dithionite-bicarbonate (CDB) and oxalate Fe and Al as well as free carbonates have all been identified with phosphate adsorption in soil and sediment systems and so deserve special notice. Only the stream sediments contained free carbonates (Table 1), with calcium carbonate equivalents as high as 12.8% for the Independence 12-1-75 sample. More striking are the differences in CDB and oxalate Fe content of the two groups of adsorbents. CDB iron in the soil samples is higher than oxalate iron, which is to be expected since the latter is presumed to remove only a fraction of the CDB iron. On the other hand, similar extractions of the bottom sediments yield higher oxalate than CDB iron values. Possible explanations for this phenomenon will be discussed later. It nevertheless points to the faulty use of the terms "amorphous" and "free oxides" of iron when referring to CDB and oxalate extracts, especially with regard to stream sediments.

Sorption Characteristics of Adsorbents

The form of the adsorption isotherm for the whole soils, clay fractions, and bottom sediments followed that of a typical Langmuir-shaped curve, as shown for the Hoytville silty clay loam, Figure 1. In every case, however, a nearly vertical leg appears in the isotherm at low c, giving the overall curve a "checkmark" shape. This phenomenon has been shown previously in published data (19,20) but was not noted since the authors presented their results in "simple" adsorption curves (x/m vs c). An adsorption curve such as this for the Hoytville soil gives some insight as to why the effect appears (Figure 2). At low final phosphorus concentrations ($<$ 0.1 ug/ml) the system buffers very strongly against increases in P concentration, as indicated by the very steep portion of the curve. The effect of this buffering is to keep c nearly constant while x/m rises rapidly, such that the ratio c/(x/m) decreases sharply at low added P. As the strong buffering region is exceeded, the simple adsorption assumes a more characteristic asymptotic shape, corresponding to the positive slope portion of the Langmuir curve. All calculations of adsorption maxima and energy parameters were determined from the slope and intercept of the Langmuir isotherm,which could be adequately represented by the single-phase form of the adsorption equation.

Table 2 shows values determined for the four sorption properties, i.e. adsorption maximum, adsorption energy, EPC, and sequentially desorbed phosphorus. The adsorption maxima fall into three distinct groups: the lowest, belonging to the surface soils; next, and not surprisingly somewhat higher, those of the clay fractions of the surface soils; last and much higher, the maxima of the bottom sediments. A second trend, which is not apparent within groups but which does show up when comparing across groups, is the roughly inverse relationship between adsorption maximum and adsorption energy. That is, the bottom sediments on average have the highest adsorption maxima but the lowest adsorption energies, while the reverse is true for the surface soils. The mean adsorption maximum of the group of bottom sediments is significantly higher than that of the surface soils at the 0.5% level (t=3.88), while the adsorption energy of the sediments is lower at the 10% level (t=2.10).

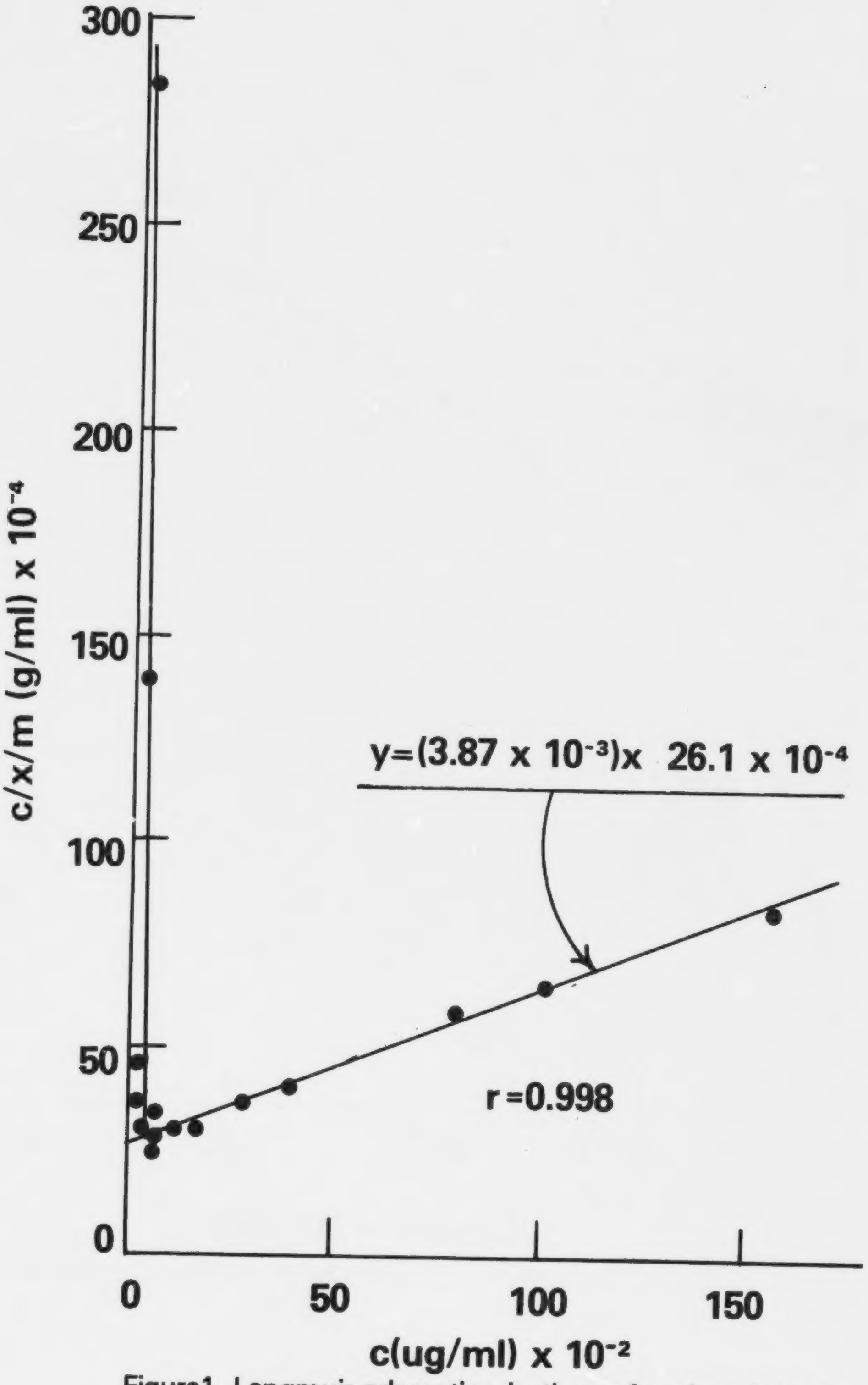

Figure1. Langmuir adsorption isotherm for phosphate on Hoytville clay loam.

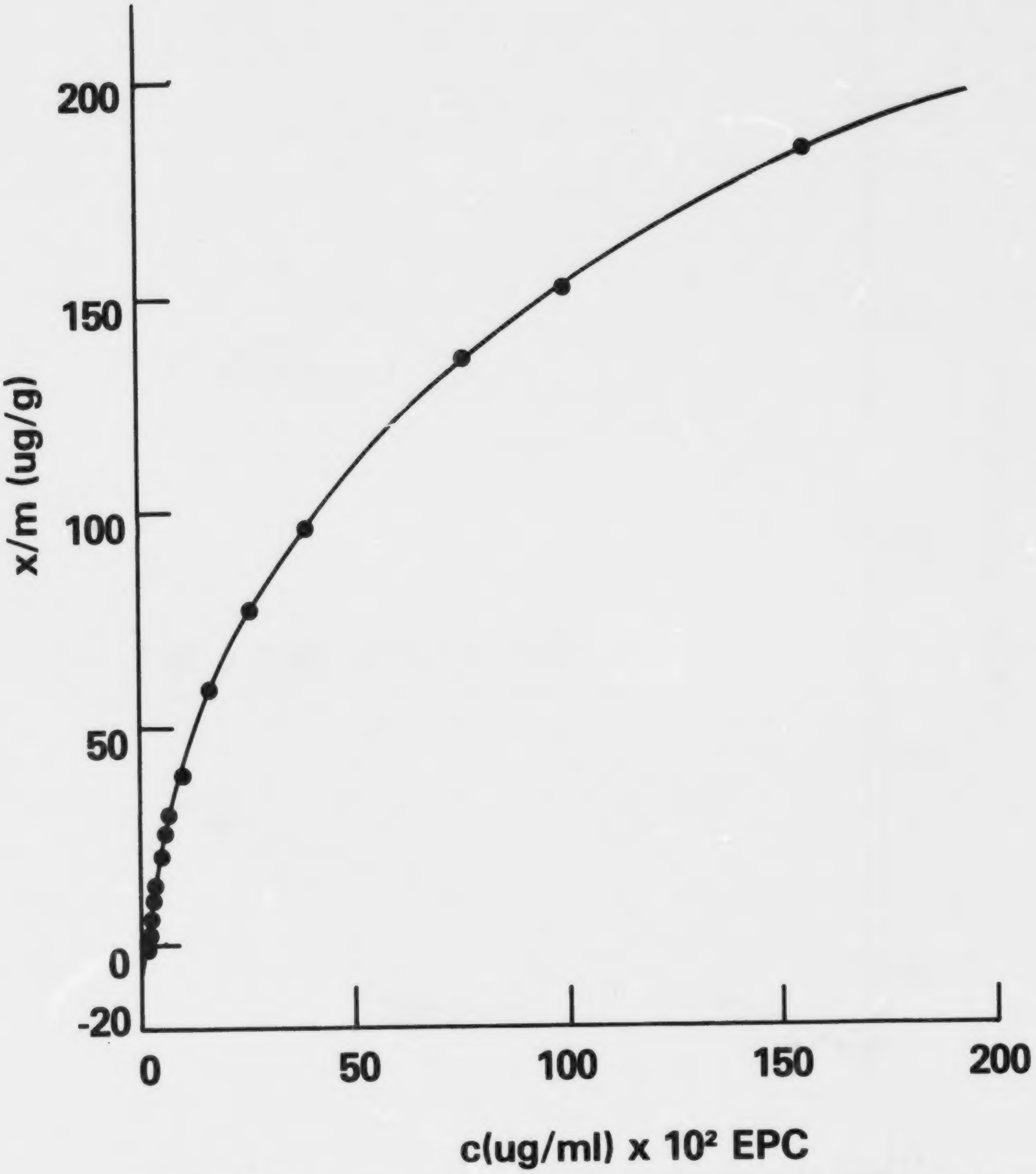

Figure 2. Adsorption isotherm for phosphate on Hoytville clay loam.

Table 2. Extractable iron, aluminum, and silicon in the soils, their clay fractions, and bottom sediments

	Amorphous Si	CDB-Fe	CDB-Al	Oxalate-Fe	Oxalate-Al
	mg/g				
Soils					
Roselms I	12.1	20.0	2.55	15.5	2.83
Broughton	10.2	21.2	2.55	6.7	2.75
Roselms II	11.6	25.0	2.35	13.3	3.33
Lenawee	12.3	17.5	3.00	15.5	5.33
Blount	12.5	32.5	4.70	16.3	3.50
Paulding	10.9	21.2	2.15	35.0	5.50
Hoytville	11.0	16.3	2.15	10.7	4.17
Soil-clay fractions					
Roselms I	11.00	17.5	1.50	16.50	1.92
Broughton	7.05	15.0	1.33	5.42	1.50
Roselms II	7.58	14.4	1.49	13.10	2.08
Lenawee	5.81	7.5	0.70	7.67	2.17
Blount	5.13	11.9	1.45	10.10	1.33
Paulding	6.46	15.0	1.15	14.30	2.42
Hoytville	4.98	9.7	0.85	6.67	2.00

Table 2. continued

	Amorphous Si	CDB-Fe	CDB-Al	Oxalate-Fe	Oxalate-Al
	mg/g				
Bottom Sediment					
Ind. 12-1-75	0.98	4.4	0.40	9.2	0.83
Aug. 12-1-75	6.63	13.8	0.95	26.0	3.00
Tiffin 12-1-75	3.17	10.0	0.70	17.7	1.83
Ind. 3-24-76	4.72	11.2	1.25	20.7	2.67
Aug. 3-24-76	6.22	13.8	1.40	27.1	3.50

Table 3. Phosphate sorption properties of the soils, their clay fractions, and bottom sediments

Adsorbent	Adsorption maximum (ug/g)	Adsorption energy (ml/ug)	EPC (ug/ml)	P desorbed (ug/g)
Soils				
Roselms I	287	1.69	0.032	1.77
Broughton	209	4.89	0.008	0.46
Roselms II	249	2.85	0.017	0.57
Paulding	216	4.35	0.140	0.29
Lenawee	244	0.80	0.060	3.58
Blount	199	2.15	0.011	0.75
Hoytville	258	1.49	0.240	0.91
Soil-clay fractions				
Roselms I clay	393	0.86	0.034	2.21
Broughton clay	323	4.15	0.016	0.95
Roselms II clay	411	1.91	0.016	0.99
Paulding clay	455	1.09	0.008	1.12
Lenawee clay	422	0.82	0.032	3.68
Blount clay	538	7.43	0.006	1.13
Hoytville clay	623	1.63	0.008	1.18
Bottom Sediment				
Ind. 12-1-75	222	1.00	0.035	3.98
Aug. 12-1-75	4870	0.68	0.054	3.61
Tiffin 12-1-75	1930	1.55	0.026	1.33
Ind. 3-24-76	3580	1.05	0.024	1.42
Aug. 3-24-76	4550	1.36	0.024	1.81

Simple product-moment correlations for the adsorption parameters of the surface soils versus selected chemical and physical properties of those soils are shown in Table 4. Only those parameters giving correlations significant at the 10% level or lower are presented. The positive relationship of adsorption maximum with total and inorganic P suggests that those soils which exhibit the highest adsorption have already retained large quantities of P from former environments and that this P is held principally in the inorganic form. A weak positive correlation of adsorption maximum with fine clay content also appears, most likely a function of the large adsorptive surface of that fraction.

Those parameters related to the stability of the complex formed between the phosphate and the surface, i.e. adsorption energy, EPC, and sequentially desorbed phosphorus, are all correlated with Bray P1 "available" P. As would be expected, the correlation with "available" P is negative for adsorption energy and positive for the other two parameters. This demonstrates that these four parameters are indicators of the same phenomena, that is, the extent to which phosphorus would be released after relatively long washing or mild acid extraction. The correlation of EPC and sequentially desorbed P with inorganic P suggests that it is this fraction which is the source of phosphorus lost from the adsorbent.

Correlations involving the clay fractions of the watershed Ap horizons are shown in Table 5. The positive correlation between adsorption maximum and organic P appears to be artifactual since no similar relationship occurs with the remaining data or is reported in the literature. The artifact may arise as a consequence of the sedimentation procedure used to fractionate the clays or their storage as a slurry in methanol and water, either of which may have altered the inorganic P content of the clay. The significant correlation of adsorption energy with CDB iron and aluminum is the first evidence that these components, which are operative in P retention by more highly weathered soils, may also be contributing to the phenomena here. Larger quantities of total and inorganic P result in more P release in the 6-hour desorption sequence, as was noted for surface soils. These last two observations imply that the desorbed phosphorus is being held by some fraction other than the CDB Fe and Al. This appears to be the case since adsorption energy and thus the stability of the phosphorus complex increases in parallel with the magnitudes of these two Fe and Al fractions.

Table 6 shows correlations of sorption parameters determined for the stream-bottom sediments with certain of their chemical and physical properties. The most striking result from the analyses is the strong positive correlation of adsorption maximum with a number of iron, aluminum, and silica fractions in the sediments. This group includes amorphous silica, oxalate Fe and Al, CDB Fe, and to a lesser extent CDB Al. Their presence together is in sharp contrast to the surface soils or clays in which none of these chemical properties were strongly correlated with adsorption maximum. It is likely that the Fe, Al, and Si fractions are associated in some type of amorphous or no more than weakly crystalline complex. Such a complex, when highly hydrated as it would be in a stream system, has a gel-like reactivity. A type of gel has been proposed as a major agent in P sorption by lake sediments since it has a very large reactive surface area with many sites for phosphate retention due to its high hydration (22,27).

Table 4. Correlation coefficients of P sorption parameters versus physical and chemical properties of the soils (n = 7)*

	Adsorption maximum	Adsorption energy	EPC	Desorbed P
Bray P1 "Available" P	n.s.	-0.868*	0.976**	0.953**
Total P	0.729	n.s.	0.768*	0.680
Inorganic P	0.809*	n.s.	0.804*	0.724
Fine clay	0.735	n.s.	n.s.	n.s.

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* Values not marked are significant at the 10% level; those marked with a "*" are significant at the 5% level; those marked with a "**" are significant at the 1% level; "n.s." indicates no significant relationship between the factors at the 10% level.

Table 5. Correlation coefficients of P sorption parameters versus physical and chemical properties of clay fractions of surface soils (n = 7)*

	Adsorption maximum	Adsorption energy	EPC	Desorbed P
CDB-Fe	n.s.	0.841*	n.s.	n.s.
CDB-Al	n.s.	0.823*	n.s.	n.s.
Total P	n.s.	n.s.	n.s.	0.706
Inorganic P	n.s.	n.s.	n.s.	0.871*
Organic P	0.741	n.s.	n.s.	n.s.
Fine clay	n.s.	-0.679	n.s.	n.s.

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* Values not marked are significant at the 10% level; those marked with a "*" are significant at the 5% level; those marked with a "**" are significant at the 1% level; "n.s." indicates no significant relationship between the factors at the 10% level.

Table 6. Correlation coefficeints of P sorption parameters versus physical and chemical properties of bottom sediments (n = 5)*

	Adsorption maximum	Adsorption energy	EPC	Desorbed P
Amorphous Si	0.997**	n.s.	n.s.	n.s.
CDB-Fe	0.972**	n.s.	n.s.	n.s.
CDB-Al	0.847	n.s.	n.s.	n.s.
Oxalate-Fe	0.981**	n.s.	n.s.	n.s.
Oxalate-Al	0.974**	n.s.	n.s.	n.s.
Bray P1 "Available" P	n.s.	n.s.	n.s.	n.s.
Total P	0.993**	n.s.	n.s.	n.s.
Inorganic P	0.960**	n.s.	n.s.	n.s.
$CaCO_3$ equivalent	-0.850	n.s.	n.s.	n.s.
Total clay	0.967**	n.s.	n.s.	n.s.
Fine clay	0.916*	n.s.	n.s.	n.s.
pH	-0.923*	n.s.	n.s.	n.s.

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* Values not marked are significant at the 10% level; those marked with a "*" are significant at the 5% level; those marked with "**" are significant at the 1% level; "n.s." indicates no significant relationship between the factors at the 10% level.

Surface-area considerations also explain the correlation of adsorption maximum with both total and fine clay content in the sediments. As was the case for the surface soils and their clays, those adsorbents which have the highest adsorption maxima appear to have retained the most P in the past. This is indicated by the highly significant correlations with both total and inorganic P. Only with the bottom sediments is pH of the adsorbent also related to adsorption - the lower pH sediments show the higher adsorption maxima, as would be expected from changes in surface charge. The reason for the negative relationship between adsorption maximum and carbonate content is not as obvious. It has been proposed in comparisons of the total phosphorus content of calcareous and non-calcareous lake sediments that carbonates are a much less energetic phosphorus retention agent than are iron and aluminum hydrous oxides (22). The carbonate fraction thus acts as a dilutant to the Fe and Al sites and so would correlate negatively with P content. Similarly, in reference to the adsorption maximum, carbonates are a less active adsorbent and effectively dilute the adsorbing capacity of the sediment.

Cross-correlations of the adsorption and desorption properties of the soils, clays, and sediments (data not presented) generally substantiate the conclusions drawn above. For the surface soils, negative correlations appear between adsorption energy and EPC, and adsorption energy and sequentially desorbed P (10%), and a positive correlation between EPC and sequentially desorbed P (1%). The implication is that both EPC and sequentially desorbed P are controlled by the stability or energy of the phosphorus-colloid complex. A less complete set of correlations appears for the soil clays and bottom sediments, but the same general trends occur: a positive correlation (5%) between EPC and sequentially desorbed P for the soil clays; and a negative correlation between EPC and adsorption energy for the stream sediments.

Differences in Phosphate Sorption

Two hypotheses may be advanced to explain the significant differences in phosphate sorption properties, especially adsorption maximum, between the watershed surface soils and the stream-bottom sediments: 1) Preferential erosion of some reactive-size fraction of the whole soil followed by further concentration of this fraction by selective transport in the stream itself;and 2) chemical alteration of the eroded soil material after deposition in the stream.

Since clays are the most reactive of the soil separates by nature of their large surface area per unit mass, the clay fractions of the surface soils were used to test the first hypothesis. As Table 3 shows, the adsorption maxima of the total clay fractions, while higher than those of the whole soils, are not even of the same order of magnitude as those of the sediments. Calculations even suggest error in the inference that the clay fraction is the only phosphorus-adsorbing medium in the soil. Expressing the adsorption maximum of the whole soil on a 100% clay basis as follows:

$$\text{maximum (100\% clay)} = \text{maximum (whole soil)} \div \text{\% clay}$$

should give a value equal to the adsorption maximum of the clay fraction. In every case, however, the calculated value exceeds the experimental, indicating the presence of other adsorbents in the whole soil besides clay. In addition, particle-size analysis of the stream sediments (Table 1) shows that they are not 100% clay at all, but generally 40 to 45% each clay and silt. The eroded and transported clay fraction cannot by itself account for all of the adsorption by the bottom sediments or even by the whole soils.

The alternate hypothesis states that alterations occur in the streambed which markedly increase adsorption capacity of the eroded soil. The chemical properties most strongly correlated with adsorption for the sediments appear to be the most likely indicators of such in situ reactions, specifically oxalate Fe and Al, CDB Fe and Al, and amorphous Si. The nature of such a complex has been mentioned previously, but its origin has not been described. The structure of iron-substituted clay minerals is largely tied to the presence of iron in the +3 oxidation state. Exposure to a redox potential only as low as +100 mv at pH 7 can reduce iron to Fe^{2+} (7), and the accompanying change in ionic radius and charge results in at least partial decomposition of the mineral. Redox potentials and pH's in bottom sediments of Maumee Basin streams have been measured as low as -371 mv at pH 7.2 (personal communication, Dr. Fred Rhoton, Agronomy Dept., Ohio State University). Upon reoxidation, iron will precipitate and may form an amorphous, highly hydrated solid phase with the structural Si and Al which were released with the reduced Fe.

The absolute quantity of amorphous material, especially iron, also suggests that alteration has occurred. Normally CDB extraction is assumed to remove all free iron and aluminum oxides, both crystalline and amorphous, while oxalate removes the amorphous fraction only. Table 2 shows, however, that in every stream-bottom sediment the quantity of oxalate iron is about twice that of CDB iron. This has been reported elsewhere in the literature (27) and suggests that the stream sediments used here have been subject to processes causing measurable changes in their structure as compared to surface soils. It is likely that most of the Fe extracted by CDB in the bottom sediments is also oxalate extractable and, in addition, oxalate may be extracting some Fe-carbonate forms such as siderite. The latter explanation is supported by the lack of free carbonate in the soils studied while the bottom sediments did contain carbonates. Substantial amounts of magnetite were recovered from several Maumee River Basin sediments (Dr. Fred Rhoton, Agronomy Dept., Ohio State University personal communication), and Gamble and Daniels (6) have reported that while magnetite had appreciable solubility in oxalate it was only sparingly soluble in CDB. Iron is released as a weathering product from soils under common ambient conditions and may find its way into streams, where it coats eroded soil particles. Groundwater is also a source of soluble iron from pedogenic processes or when it flows through iron-containing rocks and so may add to stream Fe levels.

Phosphorus Enrichment in Runoff Sediment

The total particulate P concentration of runoff sediment was estimated by subtracting filtered reactive P (FRP) from total P for runoff events where suspended solids concentration was $>$ 100 ug/ml. The calculation overestimates total particulate P, because the total P measurement contains some filtered non-reactive P which was not measured routinely in this study. However, at suspended solid concentrations $>$ 100 ug/ml, this error is not significant.

The ratio of total particulate P to total surface soil P is given in Table 7 and is compared with the clay-enrichment ratio and the P-enrichment ratio determined from the P content of the clay fractions. The P enrichment appears to be somewhat correlated with clay enrichment although clay enrichment usually underestimates P **enrichment**. The difference can be attributed to P in organic matter in finer -size fractions, and the adsorption of P from solution by sediment during transport across the field. In the interesting case of the Roselms (111) soil, there is a negative P enrichment which is supported by the lower total P content of the clay fraction versus the total soil.

It has been theorized that as erosion becomes more severe, clay-enrichment (and, therefore P-enrichment ratio) ratio decreases as more of the coarser sized particles are eroded and transported. This means that as soil loss is decreased, there will not be a proportional decrease in total P loss, since soluble P is not affected substantially by soil-loss reduction, and the sediment that is lost is the finer-textured fraction,which is highest in total P.

3.15 Conclusions

Strong contrasts appear in both adsorption and desorption behavior of the surface soils and stream sediments. Desorption, as measured by EPC and sequentially desorbed phosphorus, is not significantly different between the two groups of adsorbents. This is apparently due to low adsorption by the sediments such that their adsorbing capacities have not yet been saturated. The total phosphorus content of the sediments reflects this in that they are not appreciably higher than the phosphorus contents of the surface soils.

On the other hand, the bottom sediments have significantly higher adsorption maxima and significantly lower adsorption energies than do the surface soils. Since the total P content of the sediments is less than their adsorption capacities (except for the Independence 12-1-75), it may be concluded that they still have a large portion of their adsorption capability remaining. The sediments will act as phosphate "sponges" during transport until such time as a large enough fraction of their adsorption capacity is occupied so as to make desorption of weakly held phosphorus likely. Desorption may also become a problem if the environment of the sediment, such as pH or solution phosphorus status, changes in such a way as to destabilize the sediment-phosphorus complex. Even though only single-phase adsorption was detected for both soils and sediments in this study, the possibility is still open that a change in phosphorus status of the sediments may alter the energy of the adsorbing sites, changing their role in the phosphate balance of the stream or lake.

Future study is required to identify precisely the mechanism and nature of the changes which occur to eroded sediment after its deposition in the stream, as well as the behavior of the sediment as a phosphorus adsorbent under varying ambient conditons of redox potential, pH, and time.

Phosphorus in runoff sediment is higher than in the parent soil. This is due to the higher content of clay in runoff and possibly to sorption of soluble P by the reactive sediment during initial transport.

Table 7. Phosphorus and clay enrichment of runoff sediment

Site	% Clay		-----P content ug/g-----				Clay Enrichment	Phosphorus Enrichment	
	Soil	Runoff	Whole soil	Clay fraction	Runoff				
Roselms 111	47.0	54.2	1018	889	280	(630)*	1.15	0.28	(0.62)*
Roselms 111	-	61.2	-	-	446		1.30	0.44	
Roselms 201	42.8	47.8	554	738	1421	(734)	1.12	2.56	(1.32)
Roselms 201	-	40.8	-	-	1041		0.95	1.88	
Blount 401	22.0	46.7	450	998	1005	(1467)	2.12	2.23	(3.26)
Blount 401	-	55.1	-	-	1368		2.50	3.04	
Hoytville 611	38.9	59.8	816	1120	1591		1.54	1.95	

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* Values of runoff P content and P enrichment in parentheses are means of runoff samples from May 1975 - May 1976.

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3.2 Phosphate adsorption-desorption characteristics of suspended sediments in the Maumee River Basin of Ohio

3.21 Abstract

P adsorption-desorption characteristics of Maumee River Basin suspended sediments were compared with those of Basin soils and stream-bottom sediments. Suspended sediment contained more total P than either soils or bottom sediments. The increase in total P over soils is attributed to enrichment of P in sediment by selective erosion of fine particles and adsorption of P during fluvial transport. The suspended sediment had higher adsorption maxima than Basin soils but lower than bottom sediments and had lower adsorption energies than either soils or bottom sediments. Calcite content of the suspended sediments was positively correlated with total P, EPC (equilibrium P concentration) and P desorbed and negatively correlated with adsorption energy, implying that although calcite is a sink for P, the adsorption is weak compared with other sites for P adsorption such as hydrous oxides of Fe and Al.

3.22 Introduction

Many workers (Syers et al., 1973; Williams et al., 1971; Shukla et al., 1971) have studied the mechanisms by which P is adsorbed and retained by sediment. The dominant role of iron as an adsorption and binding site for soluble P was documented, even in calcareous sediments. Although calcite will adsorb P (Cole et al., 1953), the iron oxides have a greater capacity to do so.

In calcareous streams, secondary calcite can be formed (Wall and Wilding, 1976), probably as a result of CO_2 consumption by algae, which raises pH and shifts carbonate equilibrium toward calcite formation. Green (1977) found that calcite was formed in the Maumee River Basin in the summer when algal populations in the stream were at a maximum.[1]

The objective of this study was to study the phosphate adsorption/desorption characteristics of Maumee River Basin suspended sediments containing varying amounts of calcite and to compare these characteristics with those of watershed soils and stream-bottom sediments (McCallister and Logan, 1978).

3.23 Methods and Materials

A grab-sample approach was utilized to obtain suspended sediment samples from the Maumee River and its tributaries (Figure 1). A plastic bucket was lowered into the middle of the stream and allowed to fill without disturbing the stream floor. Approximately 40 liters of streamwater were transferred to plastic containers and transported to the laboratory for analysis. Occasionally more than 40 liters of streamwater were collected when additional suspended sediment was needed. Samples were collected on 20 different occasions during the sampling period from September 10, 1975 to September 17, 1976. Time limitations and little variation in solution and sediment characteristics of the small Maumee River tributaries made it impractical and unnecessary to collect a streamwater sample from all the sites on each sampling date during the summer months (June-September, 1976).

For the first half of the sampling period (September, 1975 - April 13, 1976), suspended sediment was concentrated by flocculation with 100 ml of 1N $MgCl_2$ per 40 liters of samples. The floccules were allowed to settle for 2 days and then the supernatant was siphoned off. The concentrated sediment was transferred to centrifuge tubes, washed with methanol and distilled water, centrifuged for 10 minutes at 1500 rpm and decanted. The washing procedure was repeated twice to ensure removal of excess salts. Samples containing more than 2g of sediment were freeze-dried and all other samples were dried by evaporation at room temperature. After April 13, 1976 the suspended sediment was allowed to settle for 4-5 days without addition of $MgCl_2$ to eliminate sample pretreatment which might affect calcite stability. The

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[1] Dan B. Green. 1977. Calcite Occurrence, Stability, and Phosphorus Interactions in the Fluvial Media Exiting the Maumee River Drainage System. M.S. Thesis. Agronomy Department, The Ohio State University.

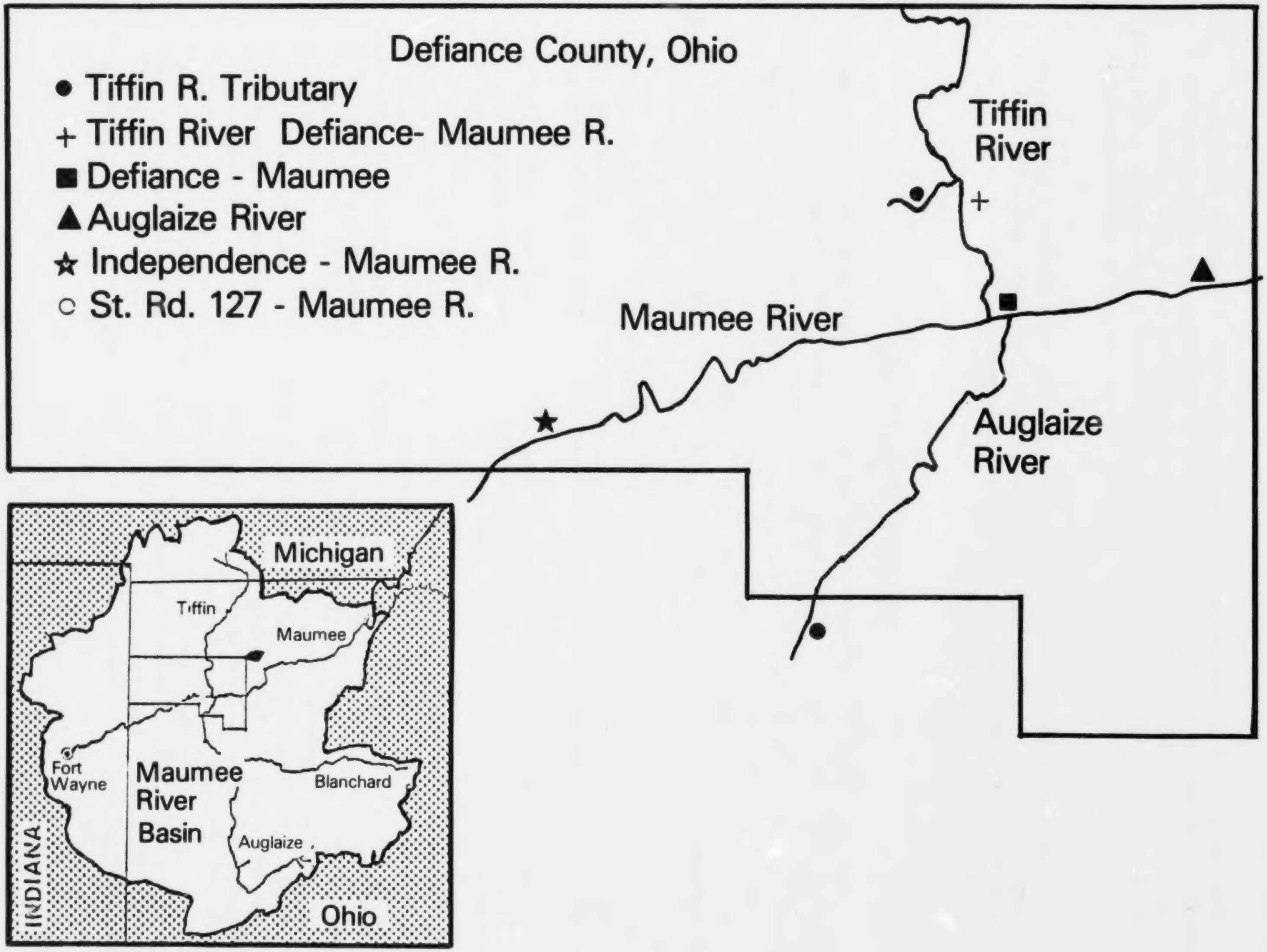
Defiance County, Ohio
● Tiffin R. Tributary
+ Tiffin River Defiance- Maumee R.
■ Defiance - Maumee
▲ Auglaize River
☆ Independence - Maumee R.
○ St. Rd. 127 - Maumee R.
Tiffin River
Maumee River
Auglaize River
Michigan
Tiffin
Maumee
Fort Wayne
Maumee River Basin
Blanchard
Auglaize
INDIANA
Ohio

Figure 1. Suspended-sediment sampling sites in the Maumee River Basin.

supernatant was siphoned off and the remaining solution evaporated at room temperature.

During periods of medium to low stream flow, the suspended sediment concentration was so low that only 1-7g of dry sediment was collected from 80 liters of streamwater. Since considerably more sediment was needed to perform routine analyses, it was necessary to composite the samples exhibiting similar stream-flow conditions and calcite content into one composite sample per site.

Calcite and dolomite were identified qualitatively by X-ray diffraction and quantitatively by gasometric analysis using a Chittick apparatus following decomposition by 6N HCl (Dreimanis, 1962). A summary of calcite content of composited samples is given in Table 1.

Phosphorus Adsorption-Desorption Study

Total P: Total phosphorus was determined by perchloric acid digestion using 0.2 g of each composite sediment sample (Sommers and Nelson, 1972). The digestion tubes were heated in a machined aluminum block to ensure uniform heating to 205°C for one hour. The cooled digest was diluted to 50 ml with distilled water, inverted several times, and allowed to settle overnight. A clear 5-ml aliquot was neutralized with 5N NaOH to a 2, 4 dinitrophenol endpoint, and the color was developed as an ascorbic acid-reduced phosphomolybdate complex (Murphy and Riley, 1962, as modified by John, 1970). The only change in the procedure was the use of 10g of ammonium molybdate per liter of stock solution to give better color stability with time. A Beckman model 24 extended-range spectrophotometer was used to read the color intensity at 730 nm, which was standardized with a digested water blank and P standards.

P adsorption: Phosphorus additons of 0, 25, 50, 100, 200, 250, 375, 500 ug were placed in 50-ml plastic centrifuge tubes, each containing 0.5g of composite suspended sediment. Also 0.5 ml of 0.05 M $CaCl_2$ and 3 drops of toluene were added to each tube to reduce the effects of unequal ionic concentrations and to reduce microbial activity, respectively. The volume was diluted to 25 ml with distilled water and placed on a rotary shaker for 24 hours at 24± 1°C. Following shaking, each sample was centrifuged at 2500 rpm for 10-15 minutes, then filtered with 0.2 um pore-size Nucleopore membranes. A 5-20 ml aliquot of each filtrate, depending on the P additions, was used for P determination (same as that used in total P procedure). The P adsorption parameters calculated from this experiment were the final concentration (c) and the amount of P adsorbed per unit of mass (x/m). From these parameters, a Langmuir adsorption isotherm was plotted (c/x/m versus c), from which the adsorption maximum (1/slope of the line) and the adsorption bonding energy (slope/y-intercept) was determined (Olsen and Watanabe, 1957; Hsu, 1964; Woodruff and Kamprath, 1965; Chen et al , 1973). The equilibrium phosphorus concentration (EPC) was determined from the plot of c versus x/m. The P concentration at x/m = 0 was taken to be the EPC (Taylor and Kunishi, 1971).

Table 1. Stream samples composited according to stream flow and calcite content of suspended sediment

Composite Sediment Sample Number	Site	Period Sampled (1976)	Stream Flow	Percent Calcite in Sediment
		Tiffin River tributary		
1	1	3/19 - 4/13	High	1.4
2	1	7/1 - 8/31	Low	7.1
3	2	2/19 - 4/13	High	1.7
4	3	2/19 - 4/13	High	3.6
5	4	2/19 - 4/13	High	2.0
		Tiffin River		
6	5	2/19 - 4/13	High	1.6
7	5	7/1 - 9/8	Low	6.0
		Maumee River tributary		
8	6	2/19 - 4/13	Med - High	1.4
9	7	2/19 - 4/13	High	1.3
		Maumee River		
10	8	2/19 - 4/13	High	3.8
11	8	7/1 - 7/15	Medium	13.3
12	8	7/20 - 8/18	Low	33.5
13	9	2/19 - 4/13	High	1.6
		Auglaize River		
14	11	2/19 - 4/13	High	2.3

P Desorption: One gram of each composite suspended-sediment sample was diluted to 25 ml with 0.5 ml of 0.5 M $CaCl_2$ (final concentration was 0.01 M $CaCl_2$), 3 drops of toluene and distilled water in 50-ml plastic centrifuge tubes. Samples were allowed to equilibrate on a rotary shaker for 6 hours, centrifuged at 2500 rpm for 10 minutes, and filtered through 0.2 um pore Nucleopore membranes. A 20-ml aliquot was color-developed and the final P concentration determined by the same procedure previously stated in P adsorption study. The preceding desorption procedure was repeated 9 times and the total P desorbed for 10 cycles was reported.

Statistical Analysis

Simple product-moment correlations were calculated between calcite content and the P parameters (total P, adsorption maximum, adsorption bonding energy, EPC, and total P desorbed) of the composite suspended-sediment samples. Correlations were also correlated among the P parameters themselves.

3.24 Results and Discussion

Phosphorus Adsorption-Desorption Characteristics

The ability to accurately predict P adsorption is dependent on data conformity to an adsorption isotherm such as the Langmuir adsorption isotherm ($c/x/m = c/b + 1/kb$) where c = equilibrium P concentration, x/m = P adsorbed per unit weight of sediment, k = constant related to bonding energy, and b = maximum amount of P adsorbed. In all cases in this study, the data did conform to the Langmuir adsorption equation by exhibiting one linear relationship between c/x/m and c. Figure 2 is representative of the Langmuir plots obtained in this study. Due to the limited quantity of sample, only 6-8 points were obtained to define the line. For a few samples, which contained high amounts of P initially, P desorption occurred at the low-equilibrium P concentrations and a "check mark"-shaped curve resulted. This has been reported and discussed by McCallister and Logan (1978). When this situation occurred, only 3-5 points defined the normal adsorption part of the curve. Due to the minimal data defining the isotherms, the Langmuir adsorption isotherm plots will only be used to indicate general trends and correlations. More specific statements concerning individual adsorption values will only be made with extreme caution.

Suspended-sediment data are given in Table 2 and are compared in Figure 3 with values obtained by McCallister and Logan (1978). In general, total P for composite suspended-sediment samples were higher than for Maumee River Basin surface soils, their clay fractions, and bottom sediments. This indicates that while P enrichment by selective erosion of the finer particles may explain some of the increase in total P, suspended sediments entering the Maumee River drainage system serve as a sink for P due to increased contact between sediment and soluble P in the fluvial system and uptake of soluble P by algae, which constitute part of the sediment, particularly at low flows. However, once deposition occurs, P may be released by the reduction of iron or decomposition of algae; this is indicated by the lower total P values for bottom sediments.

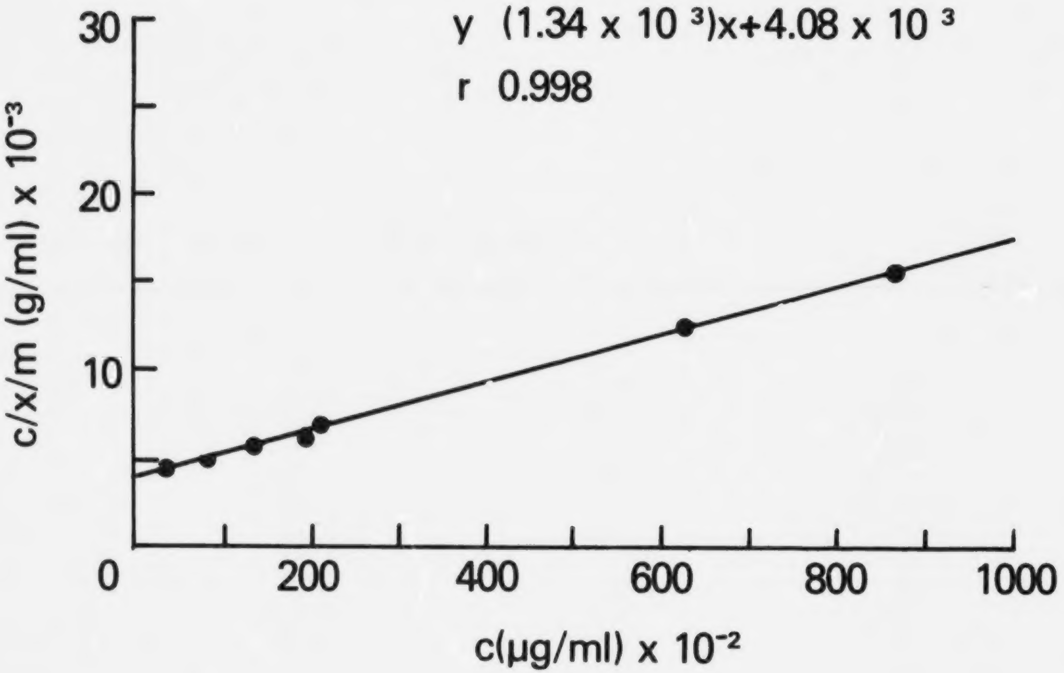

Figure 2. Langmuir adsorption isotherm of suspended sediment for phosphate.

Table 2. Total P, adsorption maximum, adsorption energy, equilibrium P concentration (EPC), and total P desorbed for stream composite suspended-sediment samples.

Composite Sediment Sample Number	Total P ug/g	Adsorption maximum ug/g	Adsorption energy ml/ug	EPC ug/ml	P desorbed ug/g
1	915	817 7	0.45	0.06	10.5
2	1080	- †	-	-	20.4
3	1085	801.7	0.44	0.05	13.4
4	1760	2063.1	0.05	0.58	93.8
5	970	510.0	0.45	0.10	9.9
6	1225	868.4	0.38	0.07	18.9
7	1420	1597.1	0.15	0.20	40.4
8	1520	878.5	0.40	0.10	17.6
9	1070	823.9	0.42	0.03	14.2
10	1075	1288.9	0.13	0.07	15.8
11	1860	1205.7	0.15	0.65	62.4
12	1890	483.1	0.11	1.01	104.8
13	1360	778.7	0.44	0.13	22.2
14	1245	744.6	0.33	0.18	37.3

† not determined because of insufficient sample

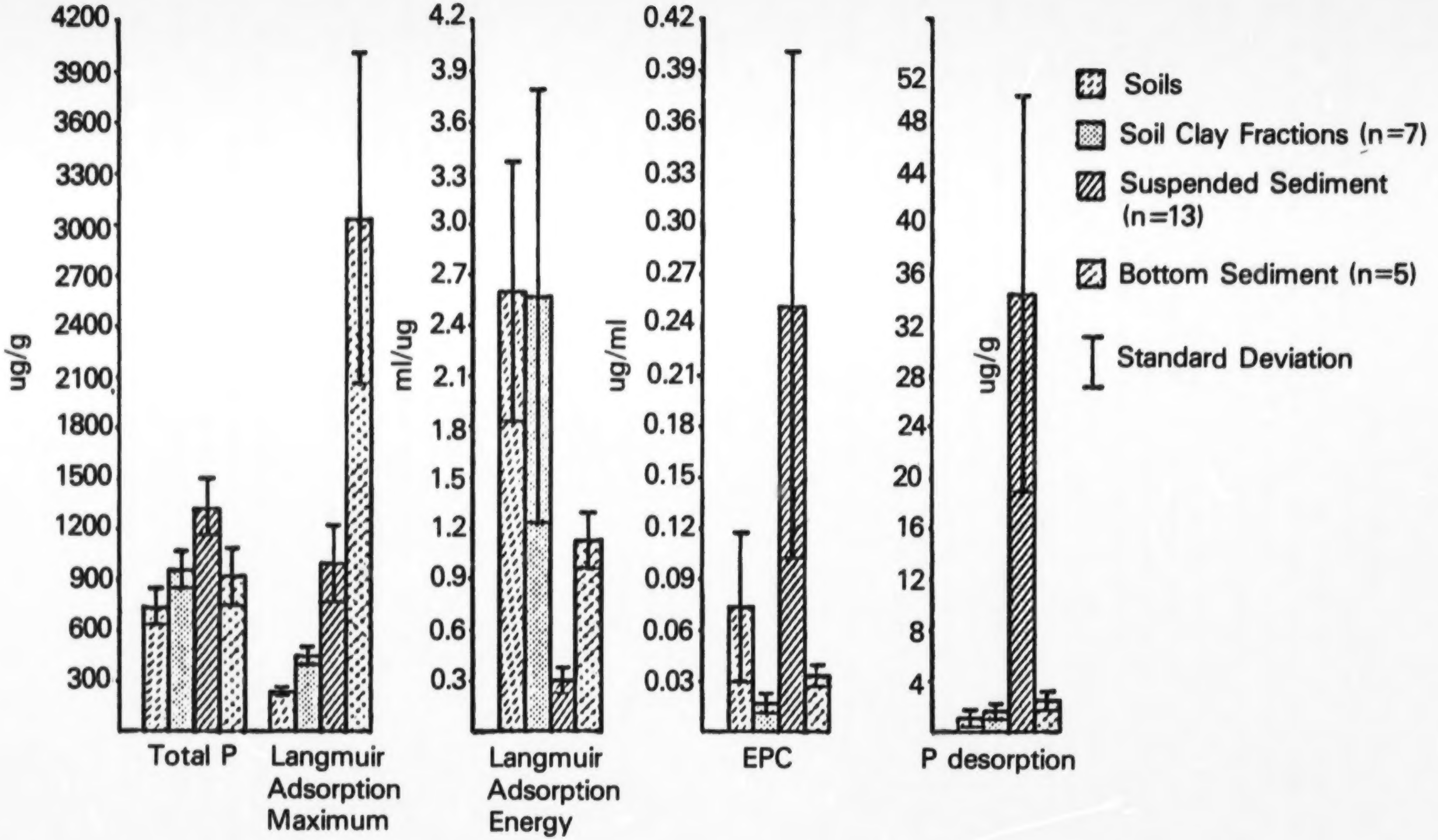

Figure 3. Adsorption/desorption characteristics of Maumee River Basin soils, their clay fractions and suspended and bottom sediments.

In general, Langmuir adsorption maxima for the composite suspended sediment samples were higher than those for the Maumee River Basin surface soils and their clay fractions, but lower than the adsorption maxima reported for bottom sediments. This implies that sediments entering the Maumee River system are altered by weathering and/or adsorption, either during transport or after deposition, in such a manner as to markedly increase adsorptive capacity. McCallister and Logan (1978) found that the content of amorphous Fe, Al, and Si in bottom sediments correlated most strongly with adsorptive capacity. Although the same mechanisms may be responsible for increasing adsorptive capacity of suspended sediments in this study, no attempt was made to verify it. Comparison between adsorption maxima and total P shows that all composite suspended-sediment samples contained more P than the quantity of P retained when the adsorption maximum is reached, except for composite suspended-sediment samples collected at sites 5, 3 and 8 (composite samples), respectively. Some of the increase in total P of the suspended sediment is a result of selective erosion and transport of clay-sized particles which contain a higher P concentration than silt and sand sized particles. However, the P content of the clay fraction of the Basin soils (Figure 3) is not high enough to account for all of the increase on the basis of clay enrichment of sediment alone. It is likely that during runoff and transport, there is some adsorption of P by the sediment. Some of the high total P for Maumee River samples (site 8) in the summer may be due to concentration of P by algae (all samples were examined microscopically for presence of algae), which were detected in these samples. The low adsorption maximum for site 8 (composite sediment) is probably due to the high calcite content and the presence of algae. Approximately 33% of the sample is calcite. All samples, however, exhibited an increase in total P above those of the clay fraction of basin soils, even those sediments that did not contain algae. Other researchers (Shukla et al , 1971; Williams et al , 1971; McCallister and Logan, 1978) have reported an inverse relationship between adsorption maxima and carbonate content,which agrees with the relationship revealed with Maumee River samples collected at Site 8 but conflicts with the relationship revealed with the Tiffin River samples that show an increase in adsorption maxima with an increase in calcite content. Therefore, this study does not conclusively demonstrate the relationship between carbonate content and P adsorption maxima.

Adsorption energy (the energy with which P in held to the adsorbent surface) of each composite suspended-sediment sample is given in Table 2. All samples had lower adsorption energies than those of the Maumee River Basin surface soils, their clay fractions, and bottom sediments from the Maumee River drainage system. This indicates that suspended sediments hold P less tenaciously than surface soils, clays,or bottom sediments. In this study, the lowest adsorption bonding energies were more frequently related to high total P rather than to high calcite content.

The equilibrium P concentration (P concentration at which adsorption and desorption is equal and is determined at the P concentration where x/m = 0) for each composite suspended sediment sample is given in Table 2. Equilibrium P concentrations reported in this study were in the same range (0.03-0.2 ug/ml) as the EPC range (0.006-0.24 ug/ml) for surface soils, clays, and bottom sediments of the Maumee River drainage system (McCallister and Logan, 1978) except for the sample collected at Site 3 and the two summer samples at Site 8 (composite samples), respectively, which show quite high (0.58, 0.65 and 1.01 ug/ml, respectively) EPC. The two Maumee River (Site 8) samples were quite high (13.3 and 33.3%) in calcite whereas the Tiffin River tributary (Site 3) sample was low in calcite (3.6%), which indicates no clear relationship between calcite content and high EPC. The three highest total P values correspond with the three highest EPC values, which indicates that high EPC is a function of total P rather than calcite content.

Results of each 10-cycle desorption are given in Table 2. The three samples collected at Sites 3 and 8 (composite samples), which exhibited high EPC and low adsorption energy yielded the highest total P desorbed (93.8, 62.4, 104.8 ug/g, respectively). Conversely, those samples with low EPC desorbed the least P. This is consistent with theory since adsorption energy, EPC, and total P desorbed are all related to the stability of the bonds formed between phosphate and sediment surfaces.

Correlations Between Calcite Content and P Sorption-Desorption Parameters

Calcite content was positively correlated (Table 3), with total P of suspended sediment indicating that calcite contributed to the adsorption of P by suspended sediment.

Calcite content was positively correlated with EPC and total P desorbed, and negatively correlated with adsorption energy parameter. All three correlations imply that whereas P content may increase with an increase in calcite content, P adsorbed by calcite is not held very strongly and can be easily desorbed.

Correlations Among P Sorption-Desorption Parameters

Total P was negatively correlated with the adsorption energy, which means that as the adsorption of P increases, the energy holding the P to the adsorbent decreases. Total P was also positively correlated with the total P desorbed and EPC that is, as the amount of P held by the absorbent increases, the quantity of P which can be desorbed increases. Similar correlations were observed by McCallister and Logan (1978) for Maumee River Basin soils and bottom sediments.

Adsorption maximum was negatively correlated with adsorption energy, which indicates that as the capacity to adsorb P increases, adsorption energy decreases. Adsorption maximum was not positively correlated with EPC and total P desorbed, which is due to the method of measuring these parameters. Total P desorbed and EPC are determined on sediments with naturally adsorbed P, whereas adsorption maxima are obtained from the Langmuir isotherm, which was developed by using P concentrations far above those naturally present in streams.

Adsorption energy was negatively correlated with total P desorbed and EPC, which is consistent with theory which predicts that as adsorption energy increases, P will be held more tenaciously and be less likely to be released.

Table 3. Correlation coefficients among phosphate parameters and calcite content from the stream-composited sediment samples (n = 13).

	Total P	Adsorption maximum	Adsorption energy	Total desorbed	EPC
Calcite content	0.674*	N. S.	-0.559*	0.759**	0.888 **
Total P		N. S.	-0.698**	0.872**	0.867 **
Adsorption maximum			-0.663**	N. S.	N. S.
Adsorption energy				-0.794**	-0.714 **
Total desorbed					0.950 **

N. S. not significant

** significant at 1% level

* significant at 5% level

Total P desorbed was positively correlated with EPC, which means that, as the capacity to release more P increases, a correspondingly higher EPC will result.

Applications of the P Sorption-Desorption Study to the Maumee River System

Relationships between calcite content and total P, and between calcite content and the bonding energy parameters (adsorption energy, EPC, and total P desorbed), can be meaningfully applied to the Maumee River system. First, when precipitation of secondary calcite occurs in the Maumee River, P adsorption capacity of the suspended sediment increases, since the quantity of total P that can be adsorbed increases. The result of this process is a reduction of the P available to algae and aquatic plants, retarding the rate of eutrophication. This is particularly significant when one considers that precipitation of calcite is favored by any process which results in reduction of CO_2 concentration in the fluvial media. During periods of rapid algae growth, CO_2 concentrations of the fluvial media are significantly reduced due to photosynthesis. Thus algal growth contributed to the precipitation of calcite, which will compete with aquatic plants for soluble P. Consequently, even though P adsorbed by calcite is not strongly bonded, as evidenced by the low adsorption energy, high EPC, and P desorption values, and calcite will be the first component to release P back into solution at low soluble P levels, calcite may be an important factor in regulating soluble P concentrations in the stream. In summary, calcite does contribute to P adsorption capacity of suspended sediments, and, even though P sorption-desorption by calcite is quite dynamic, it may significantly contribute to the role of sediment in regulating soluble P concentrations in streams.

3.25 Conclusions

Adsorption maxima for composite suspended samples were higher than those for the Maumee River Basin surface soils and their clay fractions but lower than adsorption maxima for bottom sediments from the Maumee River drainage system as reported by McCallister and Logan (1978). This implies that sediments entering the Maumee River system are altered by weathering and/or adsorption, either during transport or after deposition in such a manner as to markedly increase the adsorptive capacity. Composite suspended sediments generally contained more total P than the quantity of P retained when the adsorption maximum is reached. This is a result of P enrichment of sediment because of selective erosion of clay and also adsorption of soluble P by sediment during transport. All composite suspended-sediment samples had lower adsorption energies than the Maumee River Basin surface soils and their clay fractions or bottom sediments from the Maumee River drainage system. Equilibrium P concentrations (EPC) were in the same range as those exhibited by surface soils, clays, and bottom sediments of the Maumee River drainage system except for samples with the highest total P content. The three samples exhibiting high EPC and low adsorption energy yielded the highest total P desorbed.

Calcite content was significantly positively correlated with total P, EPC, and total P desorbed and significantly negatively correlated with the adsorption energy, which implies that calcite contributes to P adsorption capacity of suspended sediments; however, P adsorbed by calcite is quite labile. Total P was significantly correlated with the bonding energy parameters (adsorption energy, EPC, and total P desorbed), which indicates that as the amount of P held by the absorbent increases, the quantity of P in solution at equilibrium and the quantity of P which can be desorbed increases. Total P desorbed was significantly correlated with EPC, which indicates that EPC could be used to effectively estimate the amount of P which can be desorbed.

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3.3 Clay mineralogical, physical and chemical relationships between watershed soils and runoff sediments

3.31 Abstract

Runoff sediments collected at sampling stations on five small watersheds were characterized for clay mineralogy, particle-size distribution, and iron oxide content. Values for these parameters were used to determine the relationship between the watershed soils and subsequent runoff sediments.

Soil-clay mineralogy of all surface horizon samples averaged: illite 48%, vermiculite 23%, quartz 15% and expandables 14%. Comparable data for runoff sediment clay were: illite 55%, vermiculite 17%, expandables 19% and quartz 10%. Higher concentrations of illite and expandables, coupled with lower concentrations of vermiculite and quartz in the runoff sediment than occurred in the watershed soils, were attributed to preferential transport of fine clays from the soil surface.

The total clay content of the watershed soils equalled 41.8% and contained 41.3% fine clay ($<$ 0.2 um) compared to 60.2% total clay and 51.4% fine clay in the runoff sediment. Cation exchange capacity of the soil-clay fraction increased from 41 meq/100 gms. to 46 meq/100 gms. in the runoff sediment clays due the increased content of fine clays. A decrease in both amorphous iron and free iron oxide contents in runoff sediment clays was unexplained; however, preferential removal of fine clay materials may be responsible.

3.32 Introduction

Utilization of clay mineralogical data obtained from fluvial transported sediments to infer source areas can lead to erroneous conclusions. Clay mineralogy of suspended and bottom sediments from downstream sites may vary considerably from sediments obtained nearer the source area due to physical sorting and flocculation during transport.

Clay mineralogical studies relating source areas and runoff sediments collected within the watershed are scarce. Significant background information has been provided by several workers (Lund et al, 1972; Wall and Wilding, 1976; Jones et al, 1977). Wall and Wilding (1976) compared clay mineralogical data from suspended sediments and soil profiles in an attempt to identify source areas. Their results were negative as clay mineralogy of suspended sediments appeared to be a function of preferential transport, either from the soil surface or within the stream system. Jones et al (1977) monitored sediment and solution parameters in primary drainage ditches adjacent to small watersheds. Clay mineralogy data obtained from suspended sediments in the ditches differed from that of the soils. Both soil and suspended-sediment mineralogy was predominantly illitic; however, quartz was the second most abundant mineral in the sediments whereas expandable minerals were the second most abundant **group** in the soils. Wall and Wilding (1976) obtained similar results from suspended sediments collected farther downstream and listed three possible explanations: 1) preferential erosion of coarse clay from soil surfaces, which contain higher percentages of quartz than do fine clays; 2) preferential erosion of quartz from the soil; or 3) a concentration of quartz relative to the clay minerals during fluvial transport.

Lund et al (1972) found higher concentrations of montmorillonite and vermiculite in reservoir bottom sediments than occurred in surrounding soils. Mica and quartz contents were approximately equal and less than corresponding amounts in the soils. Lower amounts of quartz in the bottom sediments were attributed to sedimentation during transport,and vermiculite contents in the sediments were accounted for by source-area characteristics. Higher concentrations of montmorillonite were interpreted as: 1) fine clay enrichment in the sediments; 2) transport of truncated B-horizon soils high in montmorillonite; or 3) easily dispersed montmorillonitic soil clays.

The objective of the present study was to further explain some of the previous results by investigating the possibility of preferential transport of clay minerals from small watersheds, by analyzing runoff sediments collected at the point of entry into the stream system.

3.33 Methods and Materials

Watershed Descriptions

Runoff sediment monitoring stations were constructed on five different watersheds, four in Defiance County, Ohio and one in Wood County, Ohio (Figure 1 , page 4). Selection of a particular watershed was based on the existence of one predominant soil series in a characteristic landscape setting, which occurred extensively throughout the river basin. The soils selected for the study included: Roselms silty clay loam (Aeric Ochraqualf, very fine, mixed, mesic), Roselms silty clay loam (Aeric Ochraqualf, very fine, illitic, mesic) Blount loam (Aeric Ochraqualf, fine, illitic, mesic), Paulding clay (Typic Haplaquept, fine, illitic, non acid, mesic) Hoytville clay loam (Mollic

Ochraqualf, fine, illitic, mesic). Watershed sizes ranged from 0.32 to 3.2 hectares. For the duration of the study, soybeans were grown on the watershed following fall plowing.

Sample Collection

Runoff sediment samples originating from surface horizons were obtained by installing a Coshocton Wheel sampling device in sediment drop boxes at the mouth of each watershed. Complete details of the monitoring system are given in Volume 1 of this report. Representative soil samples were obtained from the A-horizon in each watershed by collecting an average of 15 samples using a radial fan grid method and compositing to form a single reference sample. Sampling intervals varied between slope components and soils; however, a minimum of 3 samples were collected in each delineation.

Analytical Methods

Sediment concentration (mg/l) was determined for runoff sediment samples collected at each watershed by filtering a 50 ml aliquot of the runoff using 1.0 um Nucleopore membrane. Prior to analyses, runoff sediments were concentrated by flocculation with 1.0$\underline{N}$ $MgCl_2$, washed with methanol,and dried at 40°C. Particle-size distribution was determined by the pipet method of Steele and Bradfield (1934) after dispersing with a Sonifier Cell Disruptor. Samples utilized for percent fine clay were electrolytically dispersed and fractionated according to the centrifugation procedure of Jackson (1956). Clay-size fractions ($<$ 2 um) used in all other analyses were collected by sonification and standard sedimentation procedures (Rutledge et al, 1967).

X-ray diffraction analysis utilized a Norelco diffractometer and copper radiation with a nickel K-beta filter, a 0.006-inch receiving slit, a 1° divergence slit,and a proportional counter. Sample preparation involved vacuum plating 0.15 grams of Mg-saturated, methanol-washed clay ($<$ 2 um) on a porous ceramic plate (Kinter and Diamond, 1956). Two plates were prepared for each sample; one was saturated with 10% ethylene glycol and scanned whereas the other was scanned after air drying, heating to 400°C for two hours, and heating to 550°C for two hours. Runoff sediment clays were scanned from 2° to 32° 2θ at a speed of 2° 2θ per minute. Soil clays were scanned from 2° to 32° 2θ at a speed of 1° 2θ per minute. Peak areas were delineated on the basis of symmetry and average baseline heights. Photocopies of original peaks were cut out and weighed. Relative percentages of clay minerals in each sample were determined by a modified Johns et al (1954) method.

Cation exchange capacities of the total clay fractions were determined by the sodium saturation method of Chapman (1965) after removal of organic matter with 30% H_2O_2. Amorphous iron and free iron oxide contents of the total clay fraction were obtained by atomic absorption following H_2O_2 treatment and extraction with 0.2 $\underline{M}$ ammonium oxalate (McKeague and Day, 1966) and citrate-bicarbonate-dithionite (Mehra and Jackson, 1960), respectively.

3.34 Results and Discussion

Clay Mineralogy

The clay mineralogy data from composited A-horizon soils and runoff sediments are listed in Table 1 . In most instances, little difference is noted in relative percentages between the watershed soils. Most notable is the expandable mineral content listed for the Paulding and Hoytville soils. Additionally, the Blount soil contains somewhat higher concentrations of vermiculite and lower concentrations of illite, perhaps indicating an advanced weathering state. Based on the mean values, the clay mineralogy of all sites follows the order: illite > vermiculite > quartz > expandables. The order observed for runoff sediments is: illite > expandables > vermiculite > quartz. The differences between these two orders coupled with individual runoff and soil data indicate the existence of a definite trend. As depicted in Figure 1, expandable minerals in the runoff sediment exceed the amount present in the soil. The greatest difference between the two sources occurs at the Paulding site. A slight decrease in expandable minerals is noted in the Hoytville runoff sediment relative to the soil clay; however, C-horizon materials excavated by tiling operations were left on the surface. Reference soil samples were collected in an adjacent area away from this influence, but runoff sediments may reflect contributions from lower horizons, which contain less expandable minerals (F. E. Rhoton, 1978. Clay mineralogical relationships between watershed soils, runoff, and bottom sediments in the Maumee River Basin, Ohio. Ph.D. Thesis. Ohio State Univ., Columbus). Illite percentages in the soil and runoff sediment are closer to a 1:1 relationship than any of the other mineral species but reveal a trend which is analogous to the one observed for expandables. The content of vermiculite in the runoff sediment is lower than that for the corresponding soils. Quartz varies between runoff sediments and soil in a manner similar to vermiculite, lower concentrations in the runoff sediment.

The differences between soil and runoff sediment mineralogy are not substantial in some of the watersheds considering the accuracy of quantitative mineralogy by X-ray diffraction procedures; however, identical trends exist for all watersheds. Therefore, it is suggested that the data prove conclusively that illite and expandable minerals are preferentially transported from soil surfaces, leading to an enrichment of these minerals in runoff sediments and a decrease in the percentages of quartz and vermiculite.

The previous data suggest that clay mineral abundance in the soil is the primary factor controlling runoff sediment mineralogy, as evidenced by the illitic nature of both the soil and runoff sediment clay. It is further suggested that observed differences in the mineral ratios between soil and runoff sediment clays are related to particle-size differences. Based on the data presented in Figure 1 , the relative erodibilities are: expandables > illite > vermiculite > quartz. The size ranges listed for various clay minerals include: montmorillonite (expandables) 0.01-0.1 um (Zelazny and Calhoun, 1971), illite 0.1-0.3 um (Grim, 1968), vermiculite 0.2-2.0 um (Douglas, 1977), quartz 0.2-2.0 um (Wilding et al, 1977). These size ranges correspond directly to the observed relative erodibilities.

The manner in which the clay minerals are removed from the soil surface is unknown and cannot be determined from the mineralogical data. The sediment concentration parameter was selected as a possible means of determining if transport occurs predominantly as discrete particles or as

Table 1 . Clay Mineralogy of the total clay fraction from surface soils and corresponding runoff sediments*

	---------------	---------------	---------------	%† ---------------	---------------	---------------	---------------	---------------
	Expandables		Vermiculite		Illite		Quartz	
Watershed	Soil	Sediment	Soil	Sediment	Soil	Sediment	Soil	Sediment
Roselms 1	13	14	20	17	57	60	11	9
Roselms 2	11	16	22	18	44	53	23	13
Blount	14	25	31	22	41	41	14	12
Paulding	8	19	22	16	53	60	18	5
Hoytville	23	21	21	11	45	59	11	9
Mean	14	19	23	17	48	55	15	10

* Runoff sediment mineralogy values listed represent the mean of 13, 16, 9, 15, and 27 samples for Roselms 1, Roselms 2, Blount, Paulding, and Hoytville, respectively.

† Percent of the sum of the four clay-mineral fractions.

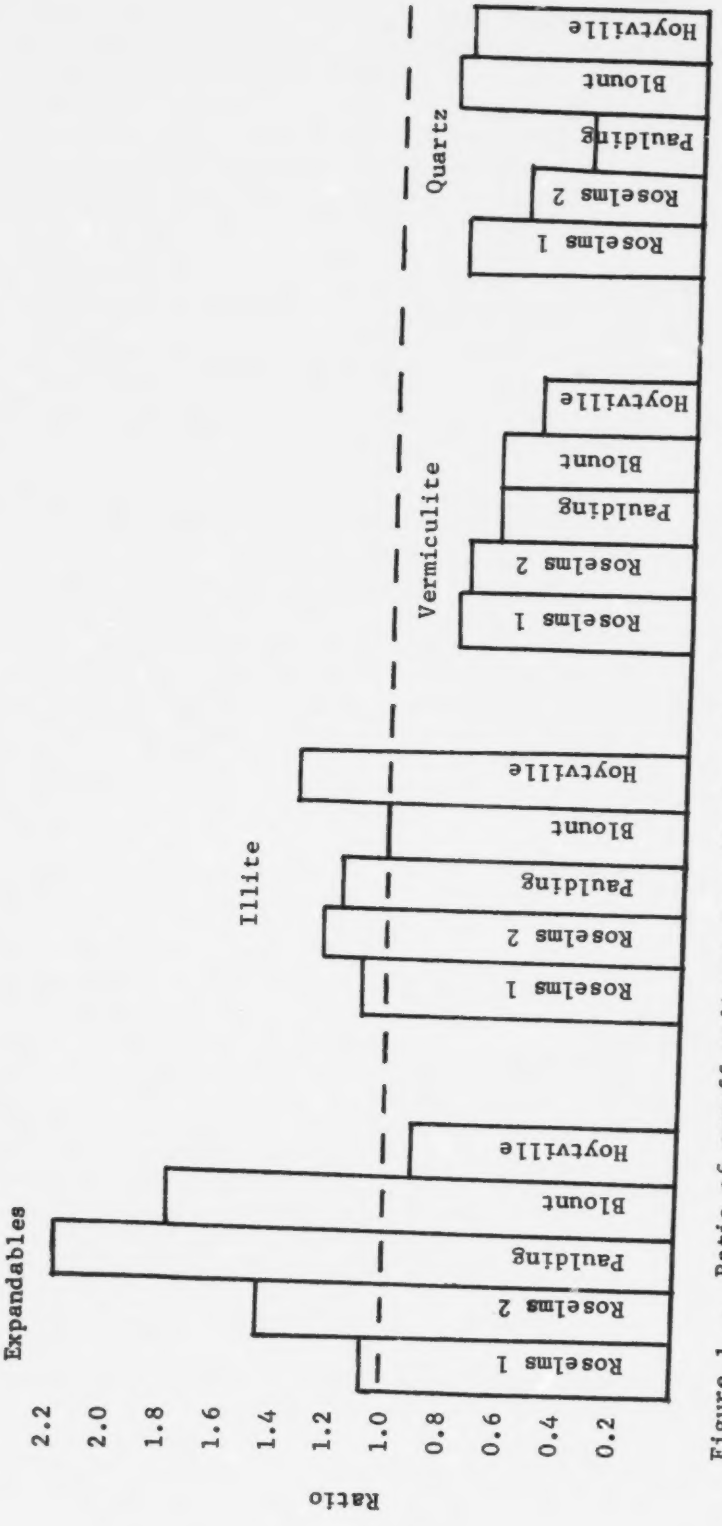

Figure 1 . Ratio of runoff sediment to soil-clay mineralogy for individual watersheds aggregates. It was assumed that clay mineralogy and sediment concentration fluctuated with rainfall intensity. Clay mineralogy was expected to be a function of rainfall intensity as it varies with particle size. Mean-particle size and sediment concentration should be positively correlated with rainfall intensity. Furthermore, expandables and illite should be negatively correlated with sediment concentration if transport occurs as individual particles, as these minerals are most concentrated in the fine clay fraction. Positive correlations between illite and expandables and sediment concentration could suggest transport in an aggregated form. Vermiculite and quartz transport as individual particles should result in positive correlations with sediment concentration, indicating removal of the coarse clay fraction.

Some of the clay-mineral variations were highly correlated with sediment concentration (Table 2), but absolute differences between high and low sediment concentrations were small. This suggests the concentration of clay minerals in the runoff sediment did not vary substantially. However, sediment concentrations used were biased toward high values, and no clay mineralogy was determined at very low sediment concentrations. A more thorough investigation is required for verification of the results.

Particle-size analyses indicated that runoff sediments contained a higher total clay concentration, 60.2% as opposed to 41.8% (Table 3) for the watershed soils. Additionally, an average of 51.4% of the total clay fraction in the runoff sediment was fine clay ($<$ 0.2 um), whereas the soil-clay fraction contained 41.3% fine clay. These figures indicate preferential removal of fine materials from soil surfaces and provide strong support for the explanations given for the differences in clay mineralogy between the watershed soils and runoff sediments. In addition to clay mineralogy, the fine clay influence on runoff sediments is evident in the recorded cation exchange capacities (Table 3). The average cation exchange capacity of the total clay fraction of the soils and runoff sediments was 41 meq/100 gms. and 46 meq/100 gms., respectively.

Amorphous iron and total free iron oxide analyses were conducted on the clay fractions ($<$ 2 um) from the soils and runoff sediments to determine how possible concentration differences between the two sources were related to preferential soil transport. Results from the analyses (Table 4) indicated that amorphous iron decreased from an average of 5.6 mg/g in the surface soils to 3.4 mg/g in the runoff sediment. Free iron oxides decreased from an average of 24.5 mg/g in the watershed soils to 18.9 mg/g in the runoff sediment. Sample pretreatment with H_2O_2 slightly increased the amount of iron extracted in each instance; however the increase did not affect the observed trends. The distribution of iron oxides between fine and coarse clays and discrete particles and clay coatings was unknown. These materials may occur as clay coatings involved in aggregate stabilization and less stable aggregates containing lower iron oxide contents are dispersed and removed; however, due to a lack of such information, the variation between soil and runoff sediment clays is unexplained.

3.35 Conclusions

The differences observed between watershed soils and their runoff sediments consisting of increases in expandable minerals and illite in addition to decreases in vermiculite and quartz in the sediment are due to preferential transport of fine clays from the soil surface. Higher concentrations of fine clay in the runoff sediment is also responsible for

Table 2 . Correlation coefficients of runoff sediment mineralogy as a function of sediment concentration †

Watershed	N	Expandables	Vermiculite	Illite	Quartz
Roselms 1	12	(-)ns	(-)ns	ns	ns
Roselms 2	15	(-).453	ns	ns	ns
Blount	9	ns	ns	(-).725*	ns
Paulding	14	.456	(-)ns	(-).380	(-)ns
Hoytville	22	ns	(-).543**	ns	ns

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† Unmarked values are significant at the 20% level; "*" indicates significance at the 5% level and "**" indicates significance at the 1% level; ns indicates not significant at the 20% level; (-) indicates negative correlation.

Table 3. Percent total clay, fine clay, and cation exchange capacity of surface soils and runoff sediments*

Watershed	Total Clay		Fine Clay		CEC (meq/100gms)	
	Soil	Sediment	Soil	Sediment	Soil	Sediment
Roselms 1	52.8	63.8	39.1	51.3	37	40
Roselms 2	34.6	55.8	34.3	45.5	39	52
Blount	27.0	58.2	38.6	50.8	41	43
Paulding	52.7	70.0	38.1	53.0	41	46
Hoytville	42.3	53.3	56.6	56.2	46	47
Mean	41.8	60.2	41.3	51.4	41	46

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* Percent fine clay and cation exchange capacity values listed for runoff sediments represent the mean of 10 samples from each watershed. Percent total clay in the runoff sediments represent the mean of 13, 18, 9, 15, and 38 samples for Roselms 1, Roselms 2, Blount, Paulding, and Hoytville, respectively.

Table 4 . Amorphous iron and free iron oxide content (mg/g total clay) of surface soils and runoff sediments*

Watershed	Amorphous Iron Soil	 Sediment	Free Iron Oxide Soil	 Sediment
Roselms 1	4.4	2.4	23.9	17.7
Roselms 2	6.2	3.1	25.0	17.2
Blount	6.8	3.7	31.2	22.4
Paulding	6.3	4.5	21.4	16.7
Hoytville	4.2	3.1	21.0	20.3
Mean	5.6	3.4	24.5	18.9

---

* Amorphous iron and free iron oxide values listed for runoff sediments represent the mean of 12, 15, 9, 15,and 24 samples for Roselms 1, Roselms 2, Blount, Paulding,and Hoytville, respectively.

increased cation exchange capacities and may explain the lower concentrations of iron oxides in runoff sediment clays. Lower concentrations of iron oxides in runoff sediment clays could partially account for the increased cation exchange capacity if present as clay coatings on soil clays.

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3.4 Coagulation and dispersion of Maumee River Basin soils and particle-size distribution of soils and sediments

3.41 Abstract

Five agricultural soils from the Maumee River Basin were dispersed by sonification in water, septic tank effluent, secondary treated wastewater, Maumee River water,and drainage ditch water. In all media except distilled water, colloids coagulated rapidly while they remained dispersed for weeks in distilled water. Of the natural media,septic tank effluent gave the least coagulation,while drainage ditch water gave the most. This was attributed to the higher concentration of sodium in septic tank effluent and higher calcium and magnesium concentrations in the ditch water.

The clay fraction of Paulding soil was dispersed by sonification in Maumee River water at different sediment concentrations. Coagulation rate increased with increasing sediment concentration. Clay dispersed in Maumee River water,diluted to 0.1, 0.2, 0.25,and 0.5 strength with distilled water, indicated that a threshold concentration of 50 ug/ml of (Ca + Mg) was needed for clay coagulation at a sediment concentration of 500 ug/ml.

Dispersion ratio of watershed soils showed that much of the fine clay and total clay were aggregated into silt and sand-sized particles.

Runoff sediment contained more clay and less silt and sand than the original soil. Sediments in tile lines were very high in clay.

3.42 Introduction

Maumee River Basin soils are, with the exception of the old glacial beach sands, very high in clay. Clay particles once detached are more easily transported than coarser silt and sand particles. During initial erosion and runoff transport, coarser particles tend to settle in the field at points where the slope decreases and water velocity is reduced. As a result, runoff sediment is higher in clay than the original surface soil from which it was eroded. Sediments in tile lines are usually also high in clay.

Under natural conditions, soil constituents do not behave as primary particles; rather, they are flocculated or coagulated into larger particles. Coagulation of primary particles, especially clays, occurs when sufficient divalent cation (usually Ca^{2+} or Mg^{2+}) is present to compress the electrical double layer surrounding primary charged particles and allow them to approach close enough for binding forces to hold them together. On the other hand, monovalent cations (especially Na^{+}) have the opposite effect and result in clay dispersion. In the soil, coagulated particles may be cemented together by agents such as organic matter and iron and aluminum oxide coatings.

The soils of the Maumee River Basin are derived from limestone till and lacustrine sediments. High in Ca^{2+} and Mg^{2+}, they are easily flocculated. River water is also high enough in Ca^{2+} to promote coagulation of suspended sediments. Domestic sewage discharges, however, are high in Na^{+} and may promote dispersion.

The objectives of this study were to:

1. Determine the relative coagulation/dispersion of Basin soils in several fluvial media
2. Determine the effect of sediment and divalent cation concentrations on clay flocculation
3. Determine the extent to which Basin soils are flocculated
4. Determine clay enrichment of runoff sediment

3.43 Methods

Soil dispersion/coagulation in natural media

Surface soil samples were taken from the same monitored watersheds as used in the other studies (Figure 1, page 4). In addition, Toledo clay from Castalia, Ohio was included.

Surface horizon samples of six different soils typical of the Maumee Basin were collected, air-dried, and crushed to pass a 2 mm sieve. The soils were classified as Blount (Aeric Ocharqualf), Hoytville (Mollic Ochraqualf), Lenawee (Mollic Haplaquept), Paulding (Typic Haplaquept), Roselms (Aeric Ochraqualf), and Toledo (Mollic Haplaquept). Particle-size distribution was determined by the sedimentation-pipet method essentially as described by Day (1965). The samples were given no pretreatments prior to dispersion. The soils were dispersed by ultrasonification with a Branson Model W185 sonifier operated with an input power of approximately 125 watts for 15 minutes per sample. An ice bath was used to keep the suspension temperature at approximately 10°C.

Organic carbon was determined by the dry-combustion method of Winters and Smith (1929). Soil pH was measured in a 1:1 slurry of soil and distilled water. Exchangeable cations (Ca, Mg, K) were measured in a 1N NH_4OAc (pH 7.0) extract with a Perkin-Elmer 303 Atomic Absorption Spectrometer. Exchangeable acidity was obtained by Ba replacement procedure of Peech et. al. (1947).

Mineralogy of the clay fraction (< 2 um) was obtained with a Norelco diffractometer equipped with a copper x-ray tube as specified by Smeck et al. (1968). Clays were Mg-saturated and given the following treatments: ethylene glycolated, air dry, heated to 400°C for 2 hours, and heated to 550°C for 2 hours. There were no pretreatments to remove carbonates, organic matter, or free oxides. Amounts of the clay minerals present were semiquantitatively estimated (±5%) by the method of Johns et al. (1954), as modified by Rutledge at al. (1975).

Natural Media

Samples of four natural media were obtained in October and November 1975 by a grab-sampling procedure. River water was collected at Independence Dam on the Maumee River near Defiance, Ohio (Figure 1, page 4); drainage ditch water came from an agricultural watershed dominated by Paulding soils in Defiance County, Ohio. Secondary-treated municipal wastewater was sampled at the Jackson Pike Wastewater Treatment Plant, Columbus, Ohio. Septic tank effluent was collected from the septic tank at Don Scott Airfield, Columbus, Ohio. Approximately 380 liters of each medium were filtered through Whatman No. 2 filter paper and stored at 4°C.

Basic cations in the media were determined by atomic absorption spectroscopy. A Corning Model 12 Research pH meter was used to determine pH. Electrical conductivities were obtained with a conductivity bridge and cell.

Each soil was dispersed in each of five different media: the four natural media plus distilled water (originally chosen to simulate rainfall or snowmelt). The suspensions had a concentration of approximately 25,000 mg/l and were dispersed by ultrasonification, according to the procedure given above. This allowed for a minimum of chemical alteration of the natural conditions and was intended to mechanically parallel dispersion by raindrop impact. The percent less than 2 um (effective diameter) fraction was determined by the sedimentation-pipet technique.

A Paulding surface-horizon sample was similarly dispersed by ultrasonification, and the clay fraction was collected through several successive steps of thorough stirring, sedimentation, and siphoning. After concentrating the clay suspension with filter candles, the approximate clay concentration was determined by filtering triplicate aliquots of the suspension through micropore filters (0.2 um diameter pores) and weighing the residues. The clay was dispersed in river water at suspended sediment concentrations of 0, 50, 100, 500, and 1000 mg/l. Coagulation was observed after stirring with an electric mixer, and it was recorded over time by photographing the sedimentation bottles. A similar series of photographs recorded the coagulation of suspended sediments at a constant concentration of 500 mg/l in river water, which was diluted with distilled water to fractional strengths of 0.1, 0.2, 0.25, 0.3, and 0.5. Temperature in both experiments was approximately 22°C.

Photomicrographs of coagulates were made according to the following procedure: Clays fractionated from the Paulding soil were suspended at several concentrations in distilled water and in river water, and the suspensions were mixed thoroughly with an electric mixer. After coagulates had begun to settle, the time elapsed since stirring was noted and a straight piece of glass tubing (4 mm diameter) was dipped into each suspension to an arbitrary but standard depth. The tube containing suspension was removed from the container, and a drop was discharged from the tip into the well of a hanging drop slide. A cover slip was placed on top, and the slide was examined under a petrographic microscope at 250X or 500X.

Soil aggregation and clay enrichment of runoff

Surface soil samples (0-15 cm) were taken from each mapping unit within each of the monitored watersheds in Defiance County (Figure 1, page 4) and composited by area weight. The Hoytville plots were also sampled and samples composited. Particle-size distribution was determined by the pipet method of Steele and Bradfield(1934) after dispersion by these methods: total dispersion in sodium hexameta-phosphate, sonification in distilled water as described previously, and dispersion by mild agitation in distilled water. In all cases, the soils were ground, screened to recover the <2 mm fraction, and dispersed without chemical pretreatment to remove organic matter or iron oxides. A dispersion ratio was calculated for each soil according to the equation:

$$\text{Dispersion Ratio} = \frac{\%\ \text{soil fraction (sand, silt or clay) by total dispersion}}{\%\ \text{soil fraction (sand, silt or clay) by water dispersion}}$$

Sediment in runoff and tile drainage from the monitored watersheds and plots were recovered by flocculating with 1N $BaCl_2$, washed in methanol and dried at 40°C. They were then dispersed by sonification in distilled water and particle-size distribution determined as described previously. An enrichment ratio was calculated using mean particle-size distribution of samples analyzed for individual events during 1975-1976 and values for the surface soils described above accoridng to the equation:

$$\text{Enrichment Ratio} = \frac{\%\ \text{runoff fraction by sonification}}{\%\ \text{soil fraction by sonification}}$$

3.44 Results

Physical, chemical,and mineralogical properties of the surface horizons of all six soils used in this study are given in Table 1. These data reveal that the soils are moderate to high in both total clay content (27-53% total clay),and base saturation (59-88%). The great majority of the exchange sites are occupied by Ca or Mg, which is primarily a reflection of the high lime content of the parent tills and lacustrine materials of northwestern Ohio. Consequently, pHs are near neutral (5.9-7.0). The clay fraction is mostly illite and vermiculite/chlorite, with secondary amounts of quartz. Such clay-mineral suites are consistent with previous unpublished investigations.

The natural media (Table 2) had alkaline pHs and, with the exception of septic tank effluent, were roughly comparable in electrical conductivity. Sodium concentrations were highly variable (probably reflecting the influence of commercial detergents), but the other cation concentrations were always of the order Ca > Mg > K. The Ca + Mg concentrations were about 100-130 mg/l. Comparison of these data with other (U.S. Dept. Interior Geological Survey, 1975) data for the respective media indicate that these values are approximately median and representative.

Total soil samples ultrasonically dispersed in distilled water remained dispersed for several weeks. On the other hand, soil samples dispersed in any of the natural media coagulated rapidly, usually within 3-7 minutes. A dispersion index was calculated by dividing the weight percent of the material with an effective settling diameter less than 2 um when the soil was ultrasonically dispersed in one of the natural media by percent total clay (determined by ultrasonic dispersion in distilled water) and multiplying by 100. In almost every case, the soils were most dispersed (least coagulated) in septic tank effluent and least dispersed (most coagulated) in drainage ditch water, with treated wastewater and river water yielding intermediate degrees of dispersion (Figure 1). Comparison of data in Table 2 and Figure 1 suggests a good correlation between sodium concentration of the suspending media and the degree of coagulation of the soil samples. Thus it appears that the sodium concentration of the fluvial media studied is a major factor controlling the degree of dispersion or coagulation of the soil samples.

There were also differences in coagulation among the six soils. The variations shown may be due in part to the degree to which the soil clays were already saturated with divalent cations on the exchange complex. The soil with the highest amount of exchangeable Ca + Mg (Paulding) coagulated most readily, and the soil with the lowest amount of exchangeable Ca + Mg (Blount) remained dispersed the longest. The other four soils were intermediate in both respects. Additionally, variability in the soils' responses to dispersion in the natural media may be attributed to the percent clay in the surface horizon. Figure 1 shows a decrease in the index of dispersion as the percent clay in the surface horizon increased. In other words, the higher the clay content, the more susceptible the soil was to coagulation in the four media.

FIGURE 1. RELATIVE DISPERSABILITY OF SELECTED SOIL SURFACE HORIZONS

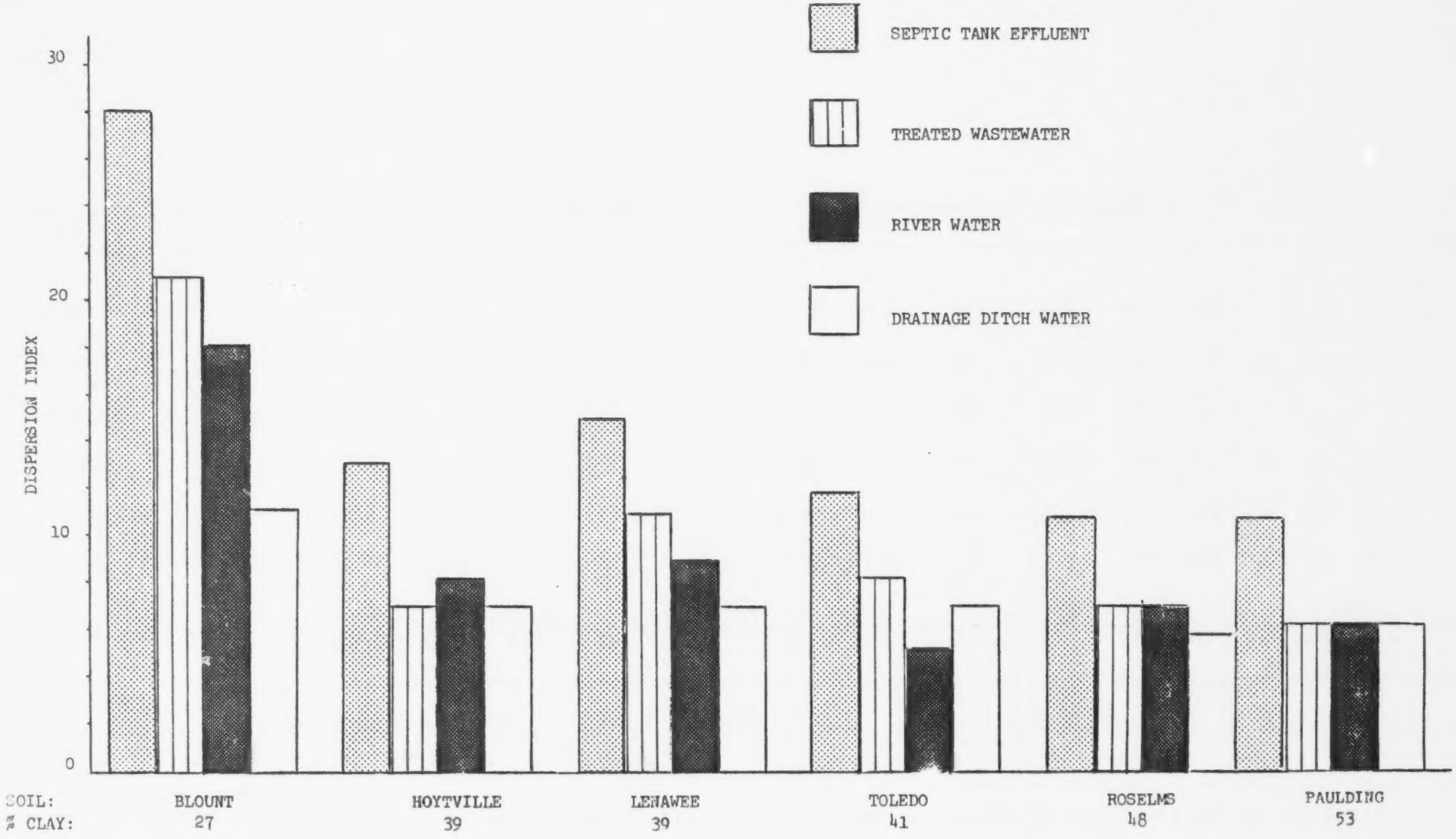

Table 1. Physical, chemical,and mineralogical properties of surface horizons from six representative soils from the Maumee Basin.

Soil	Surface depth	Particle sizes			Exchangeable cations				Base Saturation	Organic Carbon	Clay mineralogy *					pH
		sand	silt	clay	Ca	Mg	K	H			Ill	v/c	Kao	Mont	Qtz	H_2O
	cm	---------%--------			-------- meq/100g ------				%	%	----------- % -------					
Blount	20	32.5	40.1	26.8	8.1	1.7	0.29	6.9	59	1.48	36	46	T	T	14	5.9
Hoytville	25	19.4	42.0	38.6	17.8	4.5	0.61	8.7	73	2.55	63	25	T	T	7	6.7
Lenawee	23	9.9	50.8	39.3	21.3	4.9	0.53	5.0	84	2.01	51	32	T	T	12	7.0
Paulding	20	3.4	43.8	52.8	25.7	6.2	0.55	4.1	88	1.68	44	33	T	T	18	7.1
Roselms	20	72.0	44.9	47.9	15.7	7.8	1.03	8.5	74	1.91	63	26	T	T	7	6.6
Toledo	18	3.4	56.1	40.5	20.5	4.2	0.52	6.1	81	2.19	67	15	3	7	9	6.8

* Ill= illite, v/c= vermiculite and chlorite, Kao= Kaolinite, Mont=Montmorillonite, Qtz=Quartz, T=Trace

Table 2. Chemical data for natural media.

Medium	Cation concentrations						pH	Electrical conductivity at 25°C
	Na	Ca	Mg	K	Fe	Al		
	mg/l							umhos/cm
Septic tank effluent	228	70	52	20	nd	2	7.8	1852
Treated wastewater	76	58	40	14	nd	nd	7.5	840
River water	38	83	52	9	nd	nd	8.1	714
Drainage ditch water	15	86	50	15	nd	nd	7.9	746

nd = not detectable

To further examine the influence of clay concentration on coagulation, various concentrations of clays fractionated from a Paulding surface horizon were suspended in river water. A series of photographs depicting coagulation of the suspended clays over time were taken. Visual comparison of the relative turbidities of the different suspensions over time indicated that the higher the clay content the faster the suspension coagulated and settled. Both total surface area and collision frequency increase as colloid concentration increases.

A similar series of photographs revealed the influence of cation concentration in promoting coagulation of clays. River water which was diluted to various fractions of its original strength was used to suspend a constant sediment load (500 mg/l). Significant coagulation (within 16 hours) occurred only at the highest concentration of river water. We infer that the divalent cation concentration at the dispersion/coagulation threshold for a suspended sediment concentration of 500 mg/l lies in the vicinity of 50 mg/l (Ca + Mg).

Photomicrographs helped establish that the morphology of coagulates forming in clay-river water suspensions was highly variable. Some coagulates were very tightly packed and dense and had diameters of about 10-20 um. These may represent clays truly aggregated by cation suppression of double-layer repulsion. Other coagulates were fairly loose, branching networks of variable dimensions. These may be floccules or adsorption coagulates where the clay particles are linked by bridges of organic matter or hydrolyzed metal ions. An alternative explanation would be that they are simply precursors to the compact coagulates and have not yet completed aggregation.

A number of interacting environmental factors and properties of the system may encourage or confound coagulation in natural fluvial media. Results given above confirm for natural media and natural colloids the well-tested postulate that higher divalent cation concentrations are more effective than lower concentrations in coagulating colloids. It is also suggested that the high base status of the soils (particularly with respect to Ca and Mg) predisposes the soil colloids toward coagulation after their initial dispersion. Thus the critical coagulation concentration of Ca + Mg in fluvial media of the Maumee Basin may be much less than for watersheds whose soils are more acidic.

It has recently been reported by Sherard et al (1976) that erodibility of fine-textured soils in slow-moving water is positively correlated with water-extractable Na. This is somewhat comparable to our finding that natural media high in Na supported dispersion longer than media low in Na. It is speculated that future predictions of coagulation or dispersion in fluvial transport may end up incorporating (Ca + Mg)/Na ratios (or simply divalent/monvalent ratios) for the particular soils and media involved.

The concentration of suspended sediments in transport also appears to play a role in coagulation. Clays at concentrations of 500 mg/l coagulated and settled out of quiet river water after only two hours. From October 1973 through September 1974 the Maumee River at Waterville had suspended sediment concentrations considerably lower than those in headwater ditches in the Basin (Jones et al, 1977).

Waterville is also at the lower end of the Maumee drainage system, and the river's sediment load there probably already reflects the quieter waters of upstream dams and local impoundments. Wall et al (1978) showed that 34% of the clay in Maumee River Basin bottom sediments were aggregated into silt and sand-size particles.

The significance of adsorped species with respect to clay coagulation in natural media is difficult to ascertain. Soil clays are thought to be coated with adsorbed materials like organic matter and amorphous iron and aluminium oxyhyroxides or amorphous aluminosilicates. These may assist in the flocculation of soil colloids by forming bridges between the colloids,or they may simply reduce double-layer repulsions due to their presence on colloid faces. While some of the coagulates did have the three-dimensional character to be expected of floccules, no clear trends in amorphous constituents or organic carbon in the soils parallel the dispersion indices (Tables 1, 2 and Figure 1). The fact that coagulation did depend on colloid surface area in the suspension (i.e., clay concentration) strongly suggests that factors other than simply double-layer interactions are at work (Stumm and O'Melia, 1968). Whitehouse et al. (1960), in an extensive study of model clays, adsorbates, and coagulation in artificial seawater, indicated that adsorbed organic compounds may have a positive, negative, or no effect on clay-settling rates, depending on the speicies involved and the chlorinity of the medium. Since the pHs of the media studied here are probably not greater than the zero points of charge (ZPC) of amorphous oxyhydroxides or aluminosilicates (Parks, 1967), they are likely to be strongly attracted to negatively charged clay surfaces, thus encouraging coagulation.

Aggregation of clay-size sediments may be promoted by electrically heterogeneous clay surfaces. This occurs when the negatively charged faces of clay platelets are attracted to the positively charged edges of other platelets (Schofield and Samson, 1954; Bolt and Miller, 1955). The potential determining ions are again H^+ and OH^-, but in this case ZPC is probably less than pH, so this coagulation mechanism is likely not important.

The pH of the suspending medium is clearly a significant parameter affecting coagulation, as noted above. Both seasonal and daily variations occur in the river. For example, pH values as high as 9.0 (September 1974) and as low as 6.7 (January 1973) were reported for the Maumee River at Defiance, Ohio in the 1973-1974 water year (U.S. Department of the Interior Geological Survey, 1975). Daily variations were usually $<$ 0.5 pH units; pH variability would have a consequent influence on the degree of coagulation taking place. Seasonal and daily temperature differences must also be taken into account. The Maumee River at Defiance in 1973-1974 had an overall temperature range of 0-30°C, while daily temperature differences (high minus low) were usually around 2-4°C. Whitehouse et al. (1960) have reported that clay-settling rates in saline water may be decreased by about 40% when suspension temperatures are 6°C compared to 26°C.

The fact that soils and fluvial suspended sediments normally contain more than one type of clay mineral complicates greatly the study of natural coagulation phenomena. Different minerals will vary in characteristic size, isoelectric point, and surface charge density. Some studies of model systems suggest that when two or more oxides are mixed the properties and coagulating behavior of the system may be intermediate between the extremes of the individual species (e.g., Healey et al., 1973). On the other hand, Whitehouse et al. (1960) demonstrated that coagulation of clay-mineral mixtures in artificial seawater resulted in coagulates dominated by one clay mineral while material left in suspension was dominated by another. Lund et al. (1972) have hypothesized that some clay minerals in suspended sediments may be selectively coagulated in reservoirs and thus occur in higher percentages in bottom sediments than would be expected from watershed characteristics. Wall and Wilding (1976) essentially proposed the same explanation to rationalize the higher percentages of quartz in suspended river sediments on progressing down the Maumee River drainage system; they indicated that quartz must stay in suspension longer than other eroded components. Presumably the low cation exchange capacity of quartz makes it less susceptible than other clay minerals to the chemical coagulation parameters previously discussed.

Finally, turbulence of the water will influence sedimentation. While it is true that turbulence may produce more particle collisions and thus encourage coagulation, velocity gradients may still be enough to keep even dense coagulates from settling out of suspension. However, we postulate that in the relatively quiet waters of artificial reservoirs, overbank flooding, and drainage ditches of low-gradient watersheds like the Maumee, coagulation of suspended sediments is likely, depending on the chemical and physical variables given above.

Soil Aggregation

Percent sand, silt, total clay, and fine clay for the watershed soils are given in Table 3 along with their dispersion ratios. Roselms, Broughton, and Paulding soils had the highest total and fine clay contents, while Blount was lowest in clay. The sonification data gave results similar to total dispersion except that it appeared that sonification was grinding some of the sand-sized particles into smaller sizes. Water-dispersion clay contents were lower than by the other two methods, and the dispersion ratio indicated that a large percentage of the fine clay and much of the total clay is aggregated into larger particle sizes. As discussed previously, the high base status of these soils favors flocculation.

Clay enrichment in runoff and tile drainage Table 4 gives percent sand, silt, and clay by sonification for runoff and tile drainage sediments. All samples had clay contents > 55%, with the highest clay contents in the tile sediments. The enrichment ratio (Table 4) data show that the sediment contained from 1.2 to 3.6 times as much clay as the surface horizon of the soil from which it was derived. Clay content of runoff was more uniform than that of the individual soils, indicating that particle-size distribution of sediment in fluvial transport may be more a function of transport phenomena than the size distribution of the source soil material. The data also indicate that much of the coarser particles are deposited in the

Table 3. Particle-size analysis and bulk density of Maumee River Basin soils.

Site	Particle-Size Analysis of Reference Soils (%)[1]																Bulk Density (g/cm^3)	
	Total Dispersion				Sonification				Water				Dispersion Ratio					
	Total Sand	Total Silt	Fine Clay	Total Clay	Total Sand	Total Silt	Fine Clay	Total Clay	Total Sand	Total Silt	Fine Clay	Total Clay	Total Sand	Total Silt	Fine Clay	Total Clay	Field	Oven
111 Roselms	10.1	41.0	14.1	48.9	6.0	41.2	11.4	52.8	12.5	53.7	1.9	33.8	0.8	0.8	7.4	1.4	1.209	1.522
101 Roselms	14.6	50.1	4.7	35.3	10.6	49.4	5.7	40.0	17.6	59.5	0.8	22.9	0.8	0.8	5.9	1.5	--	--
131 Broughton	8.5	42.9	10.1	48.6	5.1	39.3	11.3	55.6	10.4	57.7	1.3	31.9	0.8	0.7	7.8	1.5	1.275	1.595
201 Roselms	25.3	42.3	7.3	32.4	31.6	43.8	5.5	34.6	28.5	49.4	1.1	22.1	0.9	0.9	6.6	1.5	1.328	1.564
40x Blount	32.8	42.0	6.1	25.2	27.5	45.5	4.1	27.0	34.5	47.7	0.8	17.8	1.0	0.9	7.6	1.4	1.464	1.638
50x Paulding	6.4	45.7	9.5	47.9	3.5	43.8	8.4	52.7	11.9	62.9	0.8	25.2	0.5	0.7	11.9	1.9	1.171	1.540
6xx Hoytville	19.4	43.9	6.2	36.7	16.4	41.3	6.6	42.3	24.4	53.4	1.1	22.2	0.8	0.8	5.6	1.7		

[1] Particle-size values of reference soils are weighted means of combined samples which represent all soil types within the plot. Bulk density values are from specific soil types within the plot.

Table 4. Particle-size analysis of runoff sediment (Sonification).

Site	Range			Mean			Standard Deviation			Enrichment Ratio		
	Total Sand	Total Silt	Total Clay	Total Sand	Total Silt	Total Clay	Total Sand	Total Silt	Total Clay	Total Sand	Total Silt	Total Clay
111 Roselms surface	0.0-1.2	20.1-52.8	47.0-79.7	0.3	35.9	63.8	0.3	9.5	9.6	0.1	0.9	1.2
121 Roselms surface	--	--	--	0.0	16.2	83.8	---	---	---	0.0	0.3	2.1
131 Broughton surface	0.4-2.0	16.6-32.7	66.3-83.0	1.1	24.8	74.1	0.7	6.9	7.1	0.2	0.6	1.3
201 Roselms surface	0.0-20.6	17.6-69.0	29.8-82.4	2.0	42.3	55.8	4.7	13.6	14.5	0.1	1.0	1.6
401 Blount surface	0.2-2.4	16.9-53.5	44.7-82.9	1.3	40.5	58.2	0.8	11.9	12.2	0.1	0.9	2.2
402 Blount surface	--	--	--	0.0	4.2	95.8	---	---	---	0.0	0.1	3.6
501 Paulding surface	0.0-3.8	13.6-47.3	49.5-86.2	1.3	28.8	70.0	1.4	11.3	12.2	0.4	0.7	1.3
502 Paulding tile	0.0-1.8	6.4-26.5	73.5-93.6	0.4	12.5	87.1	0.7	7.5	7.6	0.1	0.3	1.7
6x1 Hoytville surface	0.0-17.6	24.8-62.4	36.0-74.4	2.4	44.0	53.3	4.2	9.9	10.5	0.2	1.1	1.3

field and do not enter the stream system. Therefore, the 5-30% sand found by Wall et al (1978) in Maumee River Basin bottom sediments may be from streambank erosion. The high clay content of sediment in agricultural runoff illustrates why these sediments are so reactive and high in total P (McCallister and Logan, 1978).

3.45 Conclusions

The coagulation-dispersion response of soil colloids in the natural media considered here depended on the concentration of suspended clays, the degree to which they were already saturated with divalent cations, and the cation chemistry of the suspending medium. A survey of the various factors affecting natural coagulation suggests that coagulating conditions are most likely in the spring of the year, when suspended sediment concentrations are the highest, pHs are near their annual ebb, and high discharge rates from contributing watersheds produce impoundments in the drainage system. It would seem likely that clays in fluvial transport undergo multiple coagulation-resuspension events as they move from terrestrial to lacustrine environments. More detailed research is certainly needed to clarify the fate of natural soil colloids in natural fluvial systems.

Runoff sediment is higher in clay than the surface soil from which it is eroded and, in most cases, the sediment contains $>$ 55% clay.

Maumee Basin soils are aggregated with the fine and total clay aggregates to form larger particles.

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3.5 Clay-equilibration studies in natural and simulated bottom sediment environments

3.51 Abstract

Predominantly illitic soil clays were equilibrated in bottom-sediment environments under natural and laboratory conditions for 281 days and 98 days, respectively. Chemical, physical, and mineralogical parameters were monitored to identify and characterize any alterations.

Changes occurring after equilibrating for 281 days under natural conditions consisted of a reduction in carbonate contents, decrease in particle size, and a slight loss of Al and Si. No significant changes were observed in mineralogical composition.

Clays equilibrated under laboratory conditions at 4 and 25° C in either carbon dioxide, nitrogen, or air atmospheres revealed few changes other than an increase in amorphous iron. Concentrations of Al, Si, Fe, Mn, K, and Ca monitored in solution above the bottom sediments varied with the atmosphere and temperature. The concentrations of water-soluble Al and Si in solution appeared to be influenced by iron oxide coatings in the bottom sediments.

3.52 Introduction

The mode and extent of clay-mineral alteration in fluviatile sediments may be limited, but low stream gradients, high concentrations of flocculating ions,and impoundments increase the residence time of sediments and thus the possibility of alteration.

Grim (1968) states that clay minerals isolated from lake and fluviatile sediments should correspond with those from the source area, differing only due to the removal of alkali and alkaline earth components. However, other individuals (Frink, 1969; Lietzke and Mortland, 1973) have indicated that dechloritization of chloritized-vermiculite can occur when these minerals from acid source areas are equilibrated in alkaline bottom sediments. Frink (1969) further suggested that chloritized-vermiculite was converted to illite during the dechloritization process,as clay mineralogy data indicated higher amounts of illite and correspondingly lower amounts of vermiculite in the lake sediment than occurred in surrounding soils. However, the study did not relate preferential transport and differential settling of clay minerals to the assemblage observed in the sediment. Recent studies (Rhoton, 1978) have shown that clay minerals occurring in smaller particle-sizes are selectively transported from soil surfaces and can explain observed differences between bottom sediment and soil clay mineralogy. In other studies, Wall et al (1974) investigated clay-mineral alterations under laboratory conditions and concluded that geologic clays were altered under static conditions as evidenced by decreasing trends in mica, expandables and vermiculite, and increases in quartz and chlorite contents.

The present study was designed to extend previous alteration studies further through utilization of supporting data from a number of mineralogical, physical,and chemical analyses obtained before and after equilibrating clay materials in a natural bottom sediment environment and under laboratory conditions. The objectives were to determine the amount and type of clay mineral alterations occurring in bottom sediment environments and the relative contributions made by different types of equilibrating environments.

3.53 Methods and Materials

In Situ Equilibration

Twenty grams of Mg-saturated clay ($<$ 2 um) from the calcareous C-horizon of a Hoytville pedon (Mollic Ochraqualf) were placed in Plexiglas cylinders (5 cm x 20 cm). Nucleopore membranes (pore size 3.0 um) applied to **each** end by rubber O-rings contained the clay sample. This design permitted free exchange between the cell contents and the fluvial environment without any gain or loss of material. Cells were attached by spring-type clips to a plexiglas plate which was surrounded by Fiberglas screen. Scuba divers staked the plate at the sediment-water interface above Edison Power Dam on the Auglaize River, northwestern Ohio. Individual cells were retrieved by divers at intervals of 38, 148, 217,and 281 days. Cell contents were compared to reference samples using: clay mineralogy, broadening of the (001) illite peak, cation exchange capacity, percent calcite and dolomite, amorphous iron, aluminum and silica, free iron oxides, total iron, aluminum, silica and potassium, and external surface area.

Laboratory Equilibration

Approximately 3,330 grams of untreated Auglaize River bottom sediment and 13.0 liters of river water were placed in each of 10 aquariums (18.9 liter) and pre-equilibrated for one week at a controlled temperature of 4° C in one of three atmospheres: compressed air, nitrogen gas (99.9%), and 20% carbon dioxide. Four aquariums each were equilibrated with compressed air and nitrogen gas whereas the remaining two were equilibrated with carbon dioxide. Respective gases were bubbled through tygon tubing at the sediment-water interface.

Three cells containing fifteen grams of either Hoytville A or C horizon clay were partially submerged in the sediment of each aquarium following the pre-equilibration. Only calcareous C-horizon clays were equilibrated in the two carbon dioxide aquariums. Once the clay cells were in place, aquariums were sealed with Plexiglas lids.

The scheme for addition of gas into the systems was arbitrarily determined by the gas. Nitrogen gas was bubbled through the aquariums daily for 12 hours, whereas carbon dioxide was bubbled for 6 hours daily, then shut off for 18 consecutive hours. Compressed air was bubbled continuously. All aquariums were equilibrated as such for 45 days at 4° C, at which time five aquariums (2 air, 2 nitrogen, 1 CO_2) were discontinued. The remaining five were equilibrated an additional 53 days at 25° C.

Solution samples and clay cells were removed periodically at each temperature. Solution samples were withdrawn in 200 ml aliquots at a constant distance parallel to the sediment-water interface immediately following an equilibration period. One set of five aquariums was sampled frequently at 4° C (days 1, 3, 5, 7, 14, 21, 28, 45) then discarded due to depletion of solution. The other set was sampled only occasionally at 4° C(days 1, 21, 45) but more frequently at 25° C (days 49, 54, 69, 85, 98). Reference solution samples were collected from each aquarium after pre-equilibrating and immediately prior to adding clay cells. Individual clay cells were removed for analysis at approximately two-week intervals at both 4° C and 25° C. Thus, comparisons could be made of the relative temperature effects on both clay and solution parameters. All solution and clay samples were stored at 4° C until analyses were completed.

Solution parameters analyzed included: dissolved silica, iron, aluminum, manganese, calcium, and potassium. Clay samples were analyzed for amorphous iron, free iron oxides, total silica, aluminum, iron, potassium, and calcium, percent calcite and dolomite. No analyses were conducted for clay mineralogy, peak broadening, surface area, amorphous aluminum, and silica, or cation exchange capacity. Redox potential and pH measurements were made on the sediment and solution phases before clay cells were added to the aquariums; thereafter these parameters were determined only for the solution phase at the time of sampling.

Analytical Techniques

Clay samples were Mg-saturated and methanol-washed prior to and after equilibration. X-ray diffraction utilized a Norelco diffractometer, copper radiation, nickel K-beta filter, 0.006-inch receiving slit, 1° divergence slit, proportional counter, and a chart speed of 30 inches/hour. Sample preparation involved vacuum plating 0.15 grams of clay on ceramic plates

(Kinter and Diamond, 1956). Sample treatments included saturation with ethylene glycol, drying at 25° C, heating to 400° C and 550° C. Relative percentages of illite, chloritized vermiculute, kaolinite,and quartz were determined following a modified Johns et al (1954) method. Peak areas were delineated according to symmetry and average baseline heights. Photocopies of the peaks were weighed and clay mineral percentages reported as a mean of the subsamples extracted from each cell. Measurements of peak-broadening utilized the procedure of Jackson (1977).

Cation exchange capacities were determined by the sodium saturation method of Chapman (1965) after dialyzing the clays against a 10% solution of acetic acid to remove carbonates. Calcite and dolomite percentages were obtained by the Chittick apparatus (Dreimanis, 1962). Amorphous iron and free iron oxide were extracted with 0.2 M ammonium oxalate (McKeague and Day, 1966) and citrate-bicarbonate-dithionite (Mehra and Jackson, 1960), respectively,and quantified by atomic absorption. Amorphous aluminum and silica contents were determined by treating clays with boiling 0.5 N NaOH (Hashimoto and Jackson, 1960). Total silica and aluminum samples were decomposed in a Teflon bomb (Bernas, 1968) and analyzed by atomic absorption. Total iron and potassium contents were obtained by X-ray spectrographic methods. External surface area was determined by a BET method by Micrometrics Instrument Corporation, Norcross, Georgia.

Dissolved silica, aluminum, iron,and manganese were determined by the colorimetric method of Rainwater and Thatcher (1960). Dissolved potassium and calcium analyses followed atomic absorption and emission procedures. Redox potential and pH measurments were made by inserting platinum wire or glass electrodes through holes in the aquarium lids, into solution. Redox potentials were read from the millivolt scale of the pH meter.

3.54 Results and Discussion

In Situ Equilibration

The *in situ* equilibration study was designed for a duration of two years but was destroyed by flooding after 281 days. Only four cells were collected, at intervals of 38, 148, 217,and 281 days. The clay mineralogy of these samples (Table 1) reveals only slight variation with time and are well within the margin of error for such semi-quantitative analyses. In addition to time, the lack of alterations of sufficient magnitude to result in significant mineralogical changes may be due to the formation of iron oxide coatings on clay mineral surface which prevent equilibrium reactions with the river environment. Eswaran and Heng (1976) indicated that goethite coatings were effective in reducing the alteration of vermiculite and interstratified minerals.

Elemental analyses (Table 2) indicated some statistically significant (5% level) changes with time; however, absolute concentration differences are minimal in most cases. Largest changes occurred in total aluminum and silica concentrations as both decreased through 217 days. The increases after 281 days may be due to sample contamination. Absolute concentration of total iron and potassium shows little change with time.

The small increases in amorphous iron and free iron oxide contents were nonsignificant (5% level). The greatest increase in these two parameters

Table 1. Mineralogical composition of *in situ* equilibrated clays

Length of Equilibration(Days)	Chloritized Vermiculite Vermiculite	Illite	Kaolinite	Quartz
	%			
0	17	76	2	5
38	15	75	2	8
148	16	76	2	6
217	17	73	4	6
281	15	77	3	5

Table 2. Elemented and oxide analysis of *in situ* equilibrated clays

Length of Equilibration(Days)	Fe	Al	Si	K	Fe	Al	Si	Free Iron Oxides
	mg/g							
0	49.0	112.0	198.0	29.0	0.80	2.5	4.5	22.9
38	49.0	110.0	197.0	29.0	0.78	3.3	5.5	23.3
148	48.5	105.0	183.0	29.8	0.84	3.5	8.0	25.5
217	49.8	98.6	173.0	30.4	0.86	2.5	5.8	23.8
281	49.8	131.0	178.0	30.5	1.16	2.5	8.5	26.4

occurred at 281 days when FeS crystals were observed in the cell. Amorphous aluminum shows little change with time,whereas the amorphous silica concentration appeared to increase.

External surface area, cation exchange capacity,and carbonate content changes with equilibration time are listed in Table 3 . Although the increase in surface area suggests a decrease in particle size, the decrease may be influenced more by the progressive dissolution of carbonates than by clay mineral decomposition with time. The carbonate analyses indicated calcite decreased at a slightly greater rate than dolomite. Carbonate dissolution is attributed to submergence of the clay cells in the bottom sediment where the pH approximates 7.2. Calcite precipitation has been observed (Green et al, 1978) in the overlying river water where the pH ranges from 8.2-8.5. Cation exchange capacity values fluctuated considerably, indicating no time trend or correlation with the increased surface area. The erratic values may be due to incomplete carbonate dissolution by the acetic acid pretreatment.

Measurements conducted to determine the degree of peak-broadening (Table 4) were obtained from the air dry, (001) illite peak. Results indicated that broadening had occurred, which normally indicates a particle-size decrease. This suggests that the observed increase in external surface area may be related to clay-mineral degradation,which would presumably occur as a surface hydrolysis reaction disrupting the (001) reflection plane. Iron oxide contributions to the observed peak-broadening cannot be discounted since these materials were not removed prior to scanning the clays.

Laboratory Equilibration

Amorphous iron contents from the laboratory equilibrated study varied according to clay-material source (Table 5). C-horizon clays were relatively unaffected other than the increase under the CO_2 atmosphere at 25° C,whereas the amorphous iron content of A-horizon clays increased substantially, especially in the nitrogen atmosphere. The source of the increase was observed in later samples. The aquarium systems met the criteria listed as necessary for FeS formation (Connell and Patrick, 1968; Doner and Lynn, 1977). The greater increase of amorphous iron under the nitrogen atmosphere in A-horizon clays is believed to be due to lower redox potentials in the overlying water, which permitted greater concentrations of sulfide ions and ferrous iron to diffuse across the sediment-water interface. Critical redox potential measurements from the aquarium sediment were less than -300 mv. The redox potential of the solution phase in the nitrogen atmosphere eventually decreased to less than -400 mv,whereas similar measurements exceeded +300 mv for other atmospheres. The lack of any substantial increases of amorphous iron in C-horizon clay cells may be related to the carbonate material maintaining the pH near the upper limit of the FeS precipitation range.

No significant differences or trends were identified in the free iron oxide contents or in the total elemental analyses (Al, Si, Fe, Ca, K),regardless of temperatures or atmosphere. Additionally, calcite and dolomite percentages were not affected by the equilibration. All observed variations were within the analytical margin of error.

Table 3. External surface area, cation exchange capacity and carbonate analysis of *in situ* equilibrated clays

Length of Equilibration (Days)	Surface Area (meters^2/gram)	Cation Exchange Capacity (meq./100 grams)	% Carbonates	
			Calcite	Dolomite
0	46.1	25	7.0	4.0
38	N/A	29	8.2	2.3
148	48.2	24	6.6	3.0
217	51.9	20	4.9	2.8
281	51.6	39	4.9	2.4

Table 4 . Measurements of (001) illite peak broadening in *in situ* clays equilibrated for 217 and 281 days

Replication	Peak Height (mm)			Written at ½ Peak Height (mm)		
Number	Reference	217	281	Reference	217	281
1	186	149	171	5.5	5.0	5.0
2	186	132	154	4.8	4.5	5.3
3	190	142	182	5.3	4.8	5.5
4	181	128	172	5.0	5.5	5.5
5	191	139	161	4.8	5.0	5.3
6	197	141	162	4.5	5.0	5.3
7	176	147	150	4.8	5.0	5.5
8	190	141	163	5.0	5.3	5.3
9	178	158	163	5.5	5.0	5.0
10	184	138	161	4.8	5.5	5.3
Mean	185.9	141.5	163.9	5.0	5.1	5.3
Width/Height	.026	.036	.032			

Table 5. Amorphous iron content of laboratory equilibrated clays

Length of Equilibration(Days)	Temp. (°C)*	C-Horizon Clay			A-Horizon Clay†	
		N_2	CO_2	Air	N_2	Air
		mg Fe/g clay				
0	--	1.1‡			3.8‡	
14	4	1.2	1.4	1.4	4.6	3.9
28	4	1.2	1.1	1.5	4.3	4.2
45	4	1.2	1.4	1.4	4.6	3.6
69	25	1.7	2.0	1.0	6.6	4.1
85	25	1.2	1.9	1.3	6.4	5.0
98	25	1.4	2.4	1.2	8.0	5.4

---

* At the end of 45 days the temperature was increased from 4°C to 25°C.

† A-horizon clays were not equilibrated in CO_2 atmospheres.

‡ Reference value.

Concentrations of water-soluble silica, aluminum, iron, manganese, calcium, and potassium were monitored in all aquariums at both 4° C and 25° C. Redox potentials and pH were monitored simultaneously on identical solutions. Silica concentrations in solution were substantially higher under the CO_2 atmosphere than under the N_2 or air atmosphere (Figure 1) and increased considerably after the temperature was increased to 25° C (Figure 2). The air atmosphere system contained initially higher concentrations than the nitrogen atmosphere (Figure 1); however, more silica was present in the nitrogen system after 45 days. The nitrogen system also contained a higher concentration at 25° C (Figure 2), as both absolute concentration and percentage increase exceeded that of the other atmospheres.

Aluminum concentrations in solution at 4° C (Figure 3) varied in a manner similar to silica. Essentially no differences existed between the nitrogen and air atmosphere, but concentrations in the CO_2 atmosphere were exceedingly higher, increasing with time. The nitrogen gas system again exhibited the higher concentrations in solution at 25°C (Figure 4).

Silica and aluminum concentrations in solution appear to be related. Absolute concentrations and percentage increases were at a maximum in the CO_2 system at 4° C. The average solution pH for the CO_2 system was 6.2 at 4° C, compared to 9.0 for nitrogen and 8.2 for air. Initial sediment pH readings for these systems were 6.6, 7.9, and 7.6, respectively, after the one week pre-equilibration period. The lower pH reading for the CO_2 system was due to H+ production from H_2CO_3 dissociation. Since the solubility of amorphous silica is nearly constant below pH 9.0, it is assumed the increased solubility of silica in the CO_2 system is due to removal of Al from amorphous aluminosilicates, leaving silica relics which are less stable (Wildman et al, 1968).

Wilding et al (1977) indicate that metallic ion coatings, particularly Al^{3+} and Fe^{3+}, can significantly reduce the solubility of amorphous silica. Removal of Fe^{3+} coatings as reducing conditions become more intense may account for the higher concentrations of silica and aluminum in the nitrogen atmosphere at 25° C. However, increased reaction rates at 25° C and the higher pH of the nitrogen system cannot be disregarded. The higher pH is related to the production of ammonia, and hydroxyl ions released as a result of reduction of ferric and manganic compounds as the redox potential decreased (Redman and Patrick, 1965). Although the sediment pH was not monitored after the initial reading of 7.9, it is assumed that the value may have eventually approximated that of the overlying water.

Iron concentrations in solution at 4° C were low and differed little as a function of atmosphere. At 25° C, the nitrogen atmosphere affected a substantial, erratic increase, whereas concentration changes in the CO_2 and air atmospheres were slight and approximately equal (Figure 5). Manganese concentrations were too erratic to report at 4° C; however, the higher concentrations were detected in the CO_2 system. Manganese was detected in only one sample from the nitrogen system, whereas none of the air-equilibrated samples contained detectable amounts. The CO_2 system also had the greatest effect on manganese concentrations at 25° C (Figure 6), but substantial amounts were also recorded in the nitrogen system. Again, no detectable manganese was found in the air equilibrated system at 25° C.

The differences in iron concentrations between equilibrating systems appear to be strictly related to redox potential. Sufficiently low redox

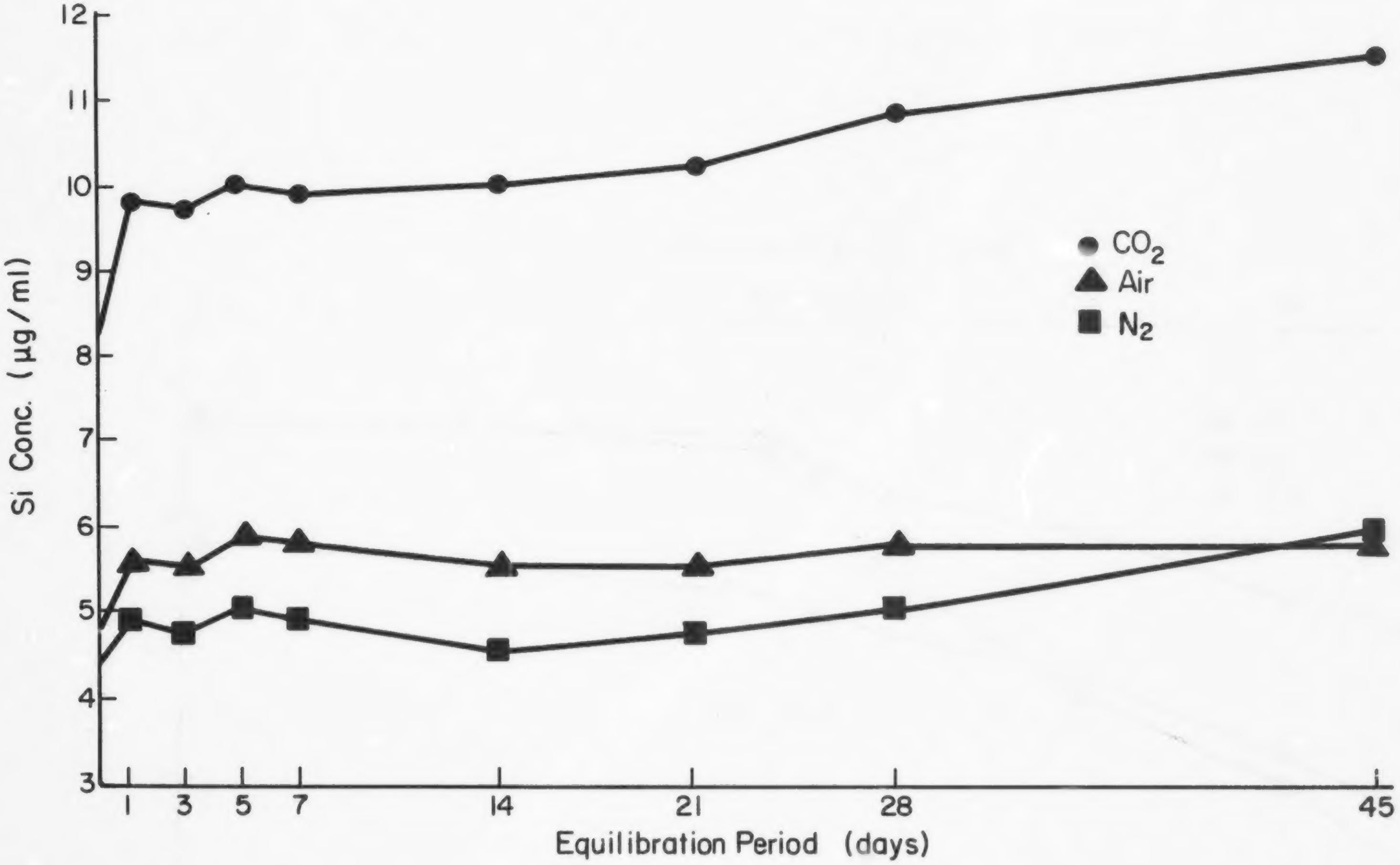

Figure 1. Concentration of water-soluble silica as a function of time and atmosphere at 4°C.

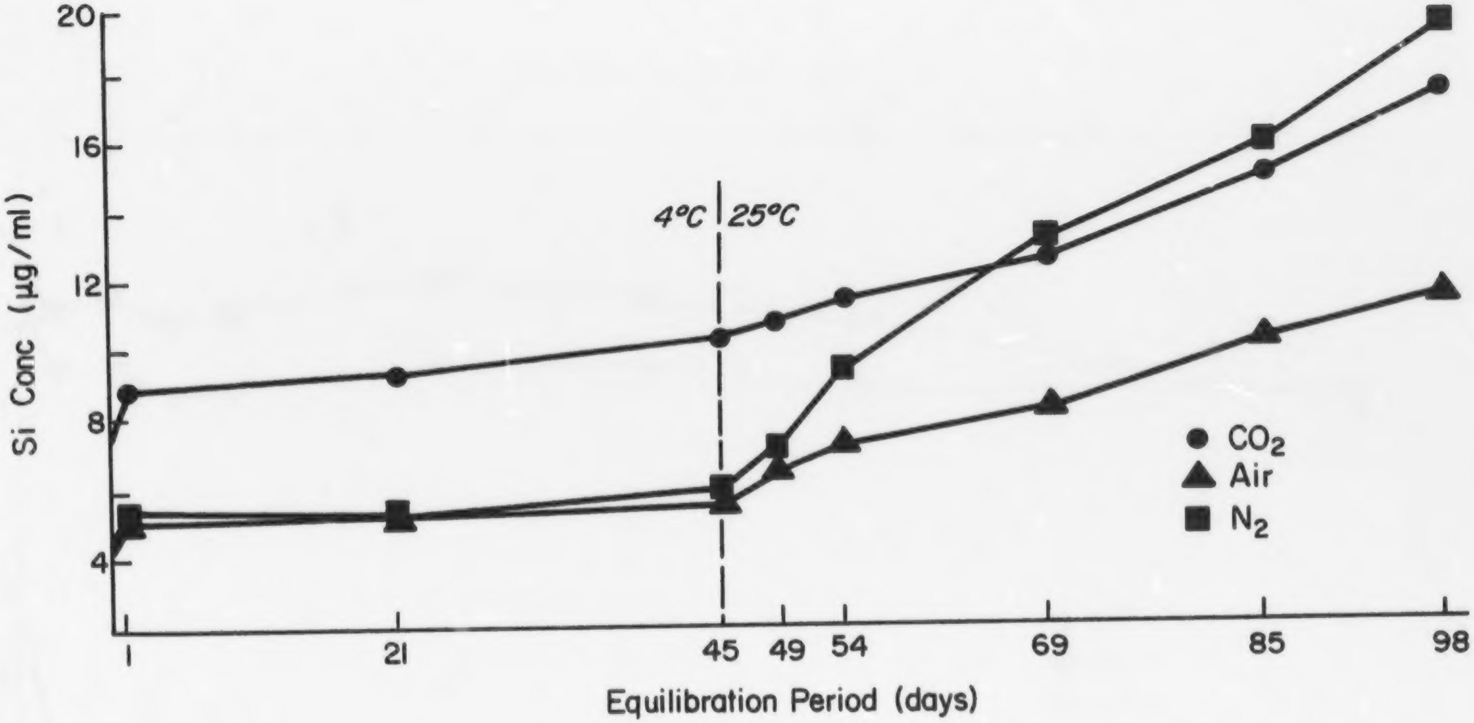

Figure 2. Concentration of water-soluble silica as a function of time, temperature, and atmosphere.

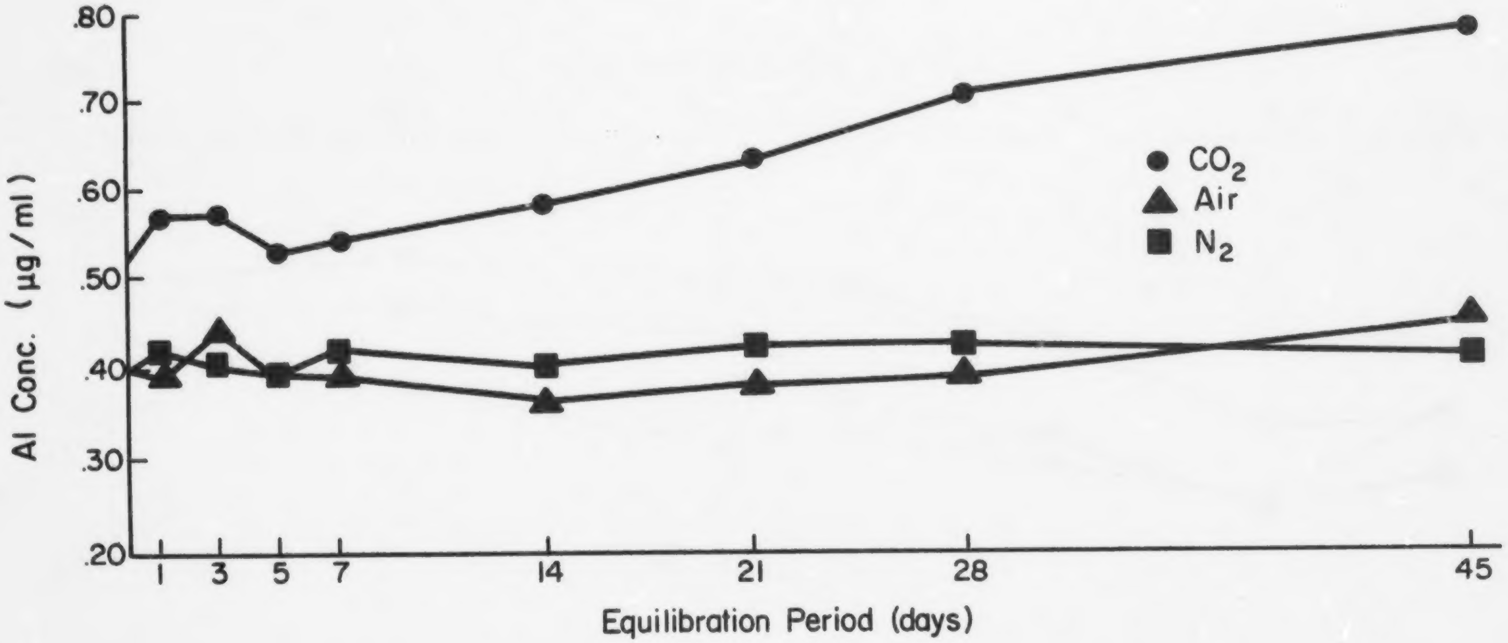

Figure 3. Concentration of water-soluble aluminum as a function of time and atmosphere at 4°C.

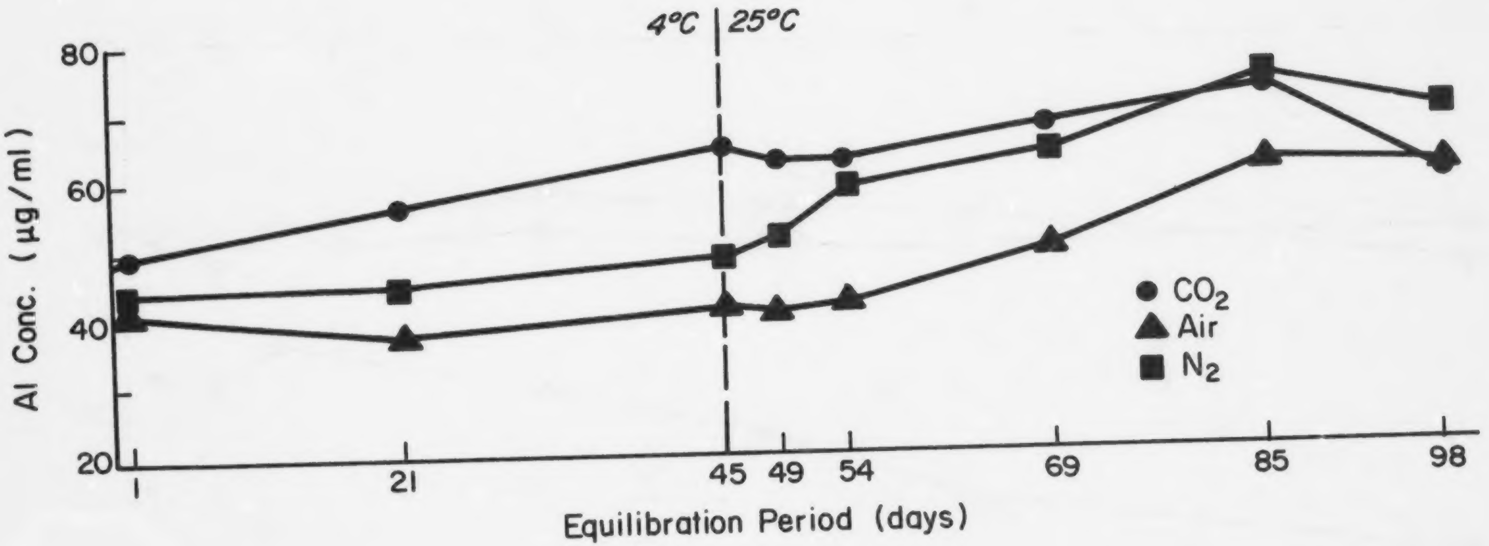

Figure 4. Concentration of water-soluble aluminum as a function of time, temperature, and atmosphere.

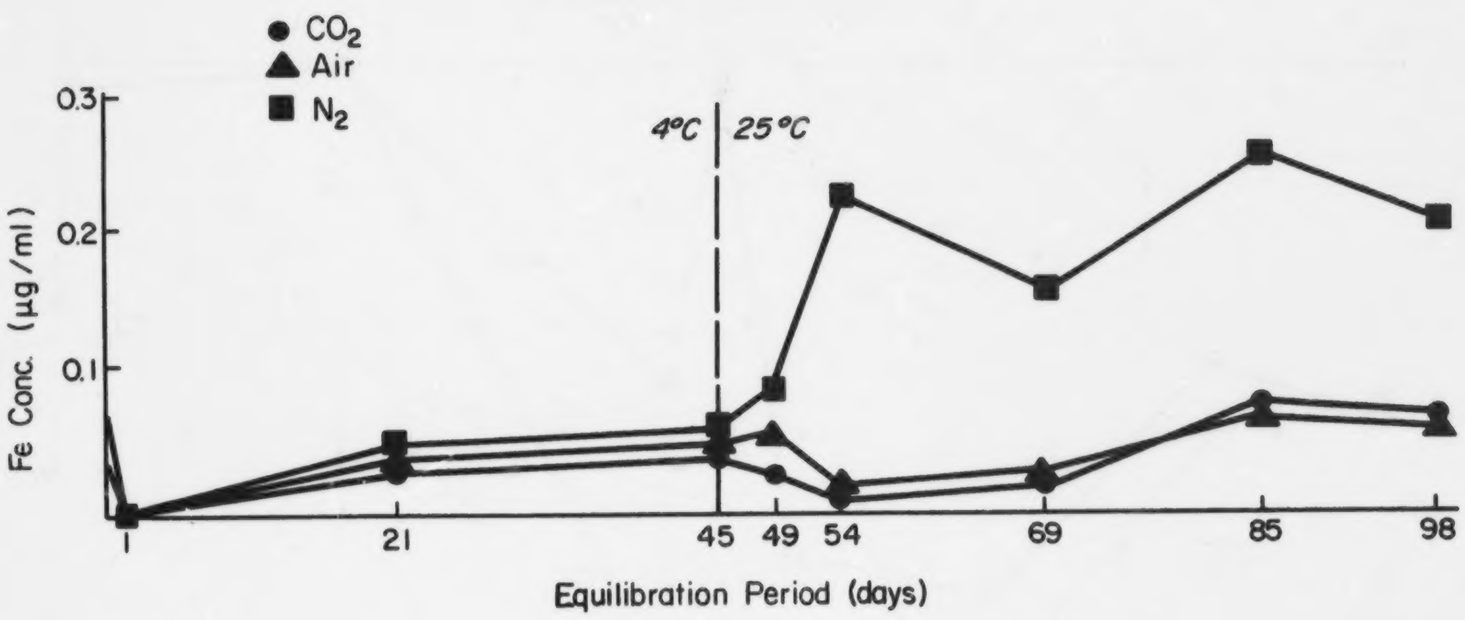

Figure 5. Concentration of water-soluble iron as a function of time, temperature, and atmosphere.

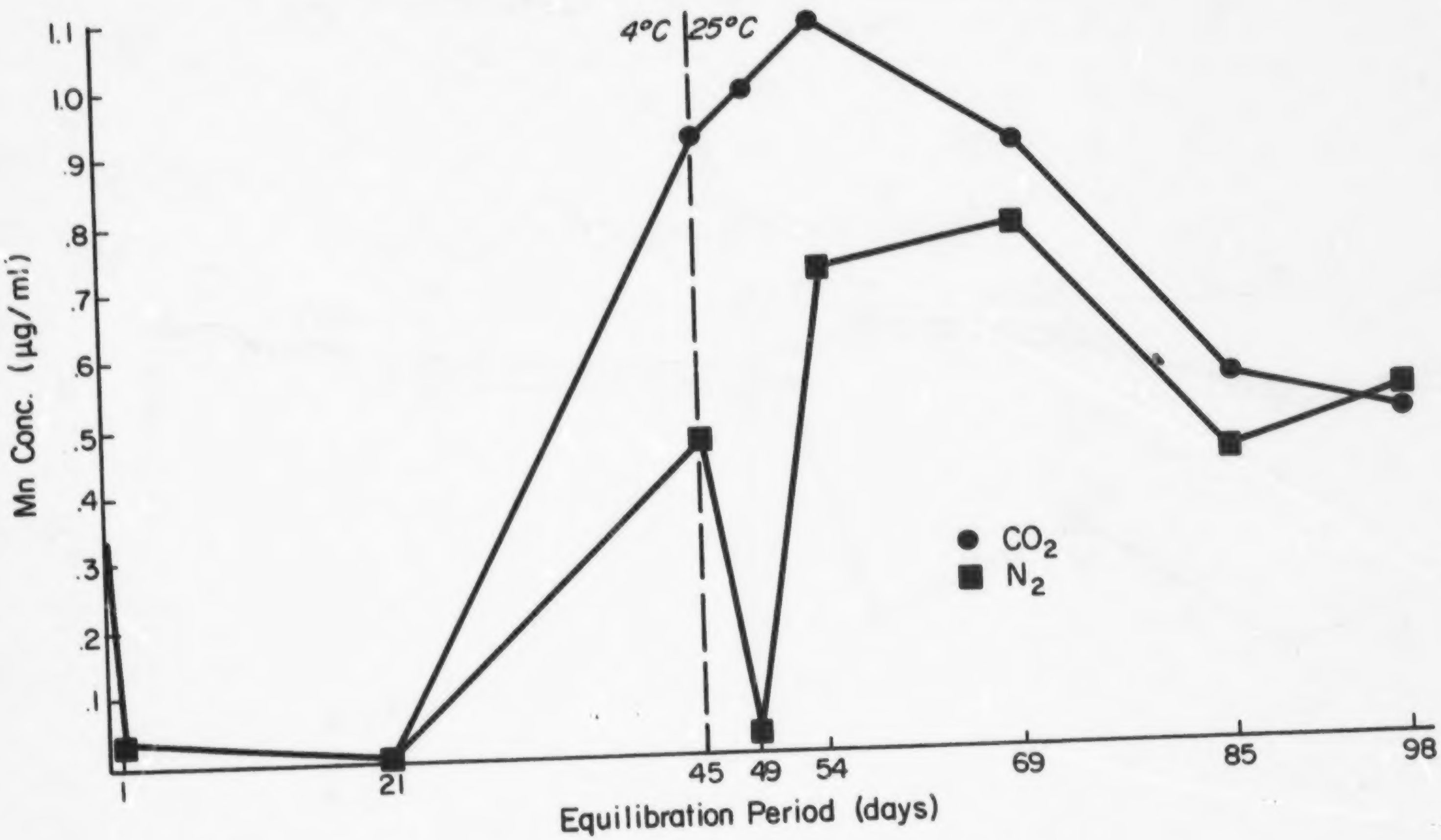

Figure 6. Concentration of water-soluble manganese as a function of time, temperature , and atmosphere.

potentials in the nitrogen system led to the reduction of ferric compounds and perhaps decreased the thickness of the oxidized zone at the interface, permitting a greater amount of iron to diffuse through into solution. The processes were greatly affected by a change in temperature, since comparable redox potentials were recorded at both temperatures but much higher concentrations existed at 25° C.

No significant differences existed for water-soluble calcium between nitrogen and air systems at either temperature; however, the CO_2 system yielded substantially higher concentrations that appeared to increase with time at both 4 and 25° C. Apparently, calcium concentrations were controlled by the dissolution rate of calcite and/or dolomite in the sediments, since the higher concentrations were associated with the lower pH values. Potassium concentrations exhibited little change with time, regardless of temperature or equilibrating atmosphere.

3.55 Conclusions

Clay-mineral alterations in freshwater bottom sediment environments are minimal when equilibrated for approximately one year. Any alterations occurring may involve surface reactions leading to particle-size reduction but not a change in basal spacings.

The existence of iron oxide coatings on amorphous aluminosilicates in bottom sediments appears to control dissolution rates and may influence clay minerals assemblages in bottom sediments.

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3.6 Occurrence and Stability of Calcite in the Maumee River

3.61 Abstract

The occurrence of secondary (precipitated) calcite and the concentrations of parameters controlling calcite dissolution-precipitation were monitored at six sites in the Maumee River drainage system during 1975-76. Secondary calcite was identified on the basis of calcite/dolomite ratios as determined by X-ray diffraction and a volumetric procedure employing the Chittick apparatus. Additional evidence for the occurrence of secondary calcite as well as crystal morphology was obtained by optical microscopy. A positive correlation between high calcium concentrations and the occurrence of secondary calcite could not be established; however, a relationship between algal blooms and calcite formation was noted. It is concluded that a reduction in the CO_2 content of the stream due to algal biomass production is the factor responsible for initiating calcite precipitation in the Maumee River system. Calcite equilibria in the stream is quite dynamic with secondary calcite appearing and disappearing in relatively short periods of time.

3.62 Introduction

The contribution of calcite, which is a common component of lake and stream sediments, to the sorption of inorganic phosphate by sediments has been examined (Shukla et al., 1971; Williams et al., 1971; McCallister and Logan, 1978, Green et al., 1978); however, little attention has been focused on the origin of calcite in sediments. In this paper, secondary calcite will refer to calcite precipitated after entry into the drainage system whereas primary calcite will refer to calcite which enters the drainage system in particulate form.

In the Maumee River drainage system of northwestern Ohio, Wall and Wilding (1976) found that the silt fraction of suspended sediments contained < 5% calcite during periods of high and medium discharge but was dominated by calcite during low flow regimes. Semi-quantitative estimates of the calcite content of the suspended silt fraction by X-ray diffraction techniques revealed that the suspended silt fraction contained up to 64% calcite during periods of low flow. Calculations indicated that the stream water was saturated with calcium carbonate; thus calcite precipitation could be expected. Determination of calcite-dolomite ratios and optical observations of the sediments with a light microscope confirmed the secondary origin of much of the calcite.

The equilibrium of calcite in an aqueous system open to the atmosphere is a function of the following: calcium (Ca^{+2}), carbonate (CO_3^{-2}), bicarbonate (HCO^-_3), hydroxide (OH^-), and hydrogen (H^+) activities and the partial pressure of carbon dioxide (PCO_2). The effect of these parameters is evident in the following reaction equation for the aqueous-carbonate system:

$$\begin{array}{c} CaCO_3 + H_2CO_3 \rightleftarrows Ca^{+2} + 2HCO^-_3 \\ \updownarrow \\ CO_2 + H_2O \end{array}$$

As temperature increases, the Ksp for calcite decreases; thus calcite solubility decreases. The relative proportions of H_2CO_3, HCO^-_3, and CO_3^{-2} in the carbonate system are a function of pH; CO_3^{-2} is the dominant species above pH 10, H_2CO_3 below pH 6.5, and HCO^-_3 between those pH values (King, 1970).

Studies of ionic concentrations in the Maumee River by Jones et al (1977) revealed that concentrations of Ca^{+2} and HCO^-_3 are also highest during low flow. Thus there appeared to be a positive correlation between high ion concentrations and calcite precipitation during periods of low flow. Our initial hypothesis in this investigation was that calcite precipitation is initiated by increasing calcium concentrations during periods of low flow due to decreasing dilution by surface runoff. Alternate hypotheses for consideration were that calcite precipitation is induced by (1) declining CO_2 contents in the fluvial media, (2) rising temperatures, or (3) increasing pH of the fluvial media. The objectives of this study were (1) to investigate the occurrence and stability of secondary calcite in stream discharge in the Maumee River Basin and (2) to determine the factors controlling the occurrence of secondary calcite in suspended sediments.

3.63 Materials and Methods.

Sample Collection

During this study, solution parameters were periodically monitored and suspended sediments collected at fourteen sites in the Maumee River drainage system. Data from only six of the sites will be discussed in this report, since secondary calcite was never detected at the sites further upstream and would thus contribute little to the testing of the hypotheses. The locations of the six sites are shown in Figure 1, page 31.

A grab-sample approach was utilized to obtain samples from the streams. A plastic bucket was lowered into the middle of the stream and allowed to fill without disturbing the stream floor. Approximately 40 liters of stream water were collected when additional suspended sediment was needed for analysis. Samples of the streams were collected on 20 different occasions during the sampling period from September 10, 1975 to September 17, 1976.

Sediment Analysis

Mineralogy: An aliquot of stream water was filtered through a ceramic plate to collect suspended sediments for X-ray analysis. After drying, the samples on the ceramic plates were irradiated with a Norelco diffractometer equipped with a copper X-ray tube as described by Smeck et al (1968). Specimens were scanned from 26° to 32° 2θ at a rate of 2° 2θ/min and plotted linearly. The time constant was one second and the counting rate was 500 counts/sec. The peaks at 29.5° 2θ and 30.8° 2θ yield a qualitative estimation of the content of calcite and dolomite, respectively.

Carbonate Content: Calcite and dolomite content and calcium carbonate equivalent of the suspended sediment were determined volumetrically with a Chittick apparatus (Dreimanis, 1962). To obtain sufficient suspended sediment for the determination of calcite and dolomite, the stream samples remaining after aliquots were removed for all other analyses was flocculated with $MgCl_2$ or simply allowed to settle for 4-5 days. The supernatant was then siphoned off. The concentrated suspended sediment was washed and dried by freeze-drying or evaporation at room temperature. Samples showing similar characteristics as determined by X-ray and optical techniques were composited for analysis.

Optical Microscopy: Immediately upon return from sampling the streams, 50 ml of stream water were centrifuged to concentrate the sediments. The concentrated sediment was permanently mounted on a microscopic slide and the abundance, size, and shape of calcite crystals were observed with a Leitz Ortholux petrographic microscope (250X magnification).

Algae Count: One-ml of each fluvial media sample was diluted with one ml of silica gel; then a 0.01 ml sample was spread over a one-cm^2 area of a microscope slide and gently heat-fixed. Fluvial media smears were stained for

3 minutes with a solution consisting of 0.20 ml of 0.5 M sodium carbonate buffer (pH 9.6), 1.1 ml of 0.01 M potassium phosphate buffer (pH 7.2), 1.1 ml of 0.85% saline, and 1.0 mg of flurescein isothiocyonate (FITC). The solution was mixed at room temperature and used immediately. The smear was then washed in 0.5 M sodium carbonate buffer (pH 9.6) for 10 minutes and in 5% sodium pyrophosphate for 2 minutes (Babiuk and Paul, 1970). The smears were immediately mounted in glycerol and observed with a Leitz-Ortholux microscope equipped with a super-pressure mercury lamp-HBO 200W L1 Green. At a magnification of 675X, the total number of algal cells per field was recorded. The average number of algal cells for 20 random fields was used to calculate the algal cell concentration (algal cells per 1 ml of fluvial media).

Solution Analysis

Calcium: Calcium was determined by atomic adsorption using a Varian Techtron AA6 Atomic Adsorption Spectrophotometer. A 25-ml filtered aliquot of drainage water was diluted to 50 ml with 2.5 ml of 1,000 mg/l lanthanum solution and distilled water. Standard solutions were prepared to calibrate the spectrophotometer. The concentrations (mg/l) of calcium were read directly from the spectrophotometer.

Electrical Conductivity: A conductivity bridge and cell was used to determine the electrical conductivity of the stream sample (Richards, 1954).

pH: The pH was determined on a Beckman Expandomatic SS-2 model pH meter.

Bicarbonate: HCO_3^- concentrations in the water sample were determined by titration with dilute (0.01-0.03 N) H_2SO_4, using bromphenol blue as the endpoint indicator (Jackson, 1958).

3.64 Results and Discussion

Characteristics of Fluvial Media

Tributaries of the Maumee River tended to yield higher concentrations of calcium and bicarbonate and higher electrical conductivities than the main stem. Median concentrations of calcium and bicarbonate and electrical conductivities ranged from 68 to 74 mg/l, 135 to 216 mg/l, 520 to 721 umhos/cm, respectively, for tributaries of the Maumee River, whereas the three sampling sites in the Maumee River yielded values ranging from 48 to 57 mg/l, 152 to 181 mg/l, and 509 to 566 umhos/cm for these parameters, respectively (Table 1). These values are similar in magnitude to those reported by Jones et al (1977) for the Maumee River at Waterville which is farther downstream.

Little importance was placed on measurement of temperature and pH due to the narrow range encountered in previous studies (Jones et al , 1977). Thus initial measurements of these parameters were not obtained; however, to provide some indication of their magnitude and variability, temperature and pH were monitored during August and September, 1976. Both temperature and pH were

TABLE 1. TEMPERATURE, pH, CALCIUM, BICARBONATE, AND ELECTRICAL CONDUCTIVITY VALUES OF THE MAUMEE RIVER DRAINAGE SYSTEM (SEPTEMBER 1975 TO SEPTEMBER 1976)

		Site					
		Tiffin R. Tributary	Tiffin River	Maumee River St. Rd. 127	Auglaize River	Maumee River Independence	Maumee River Defiance
Calcium (mg/l)	Minimum	30	32	32	53	31	39
	Maximum	86	95	81	71	66	68
	Median	72	74	53	68	57	48
Bicarbonate (mg/l)	Minimum	112	124	129	117	105	104
	Maximum	285	286	280	166	218	200
	Median	206	216	156	135	181	152
Electrical Conductivity (µmhos/cm)	Minimum	243	259	302	551	471	472
	Maximum	632	714	569	826	775	653
	Median	520	577	509	721	566	510
pH*	Minimum	7.9	8.0	8.5	8.3	8.1	8.4
	Maximum	8.1	8.0	9.1	8.7	9.0	8.9
	Median	8.0	8.0	8.9	8.5	8.7	8.6
Temperature* (°C)	Minimum	17	19	23	19	22	22
	Maximum	22	23	28	23	28	27
	Median	20	21	24	22	24	23

* Temperature and pH were only monitored during August and September of 1976.

slightly higher in the Maumee River than its tributaries. Median temperature and pH ranged from 20 to 22°C and 8.0 8.5, respectively, for tributaries of the Maumee River, whereas these parameters ranged from 23 to 24°C and 8.6 to 8.9, respectively, for the Maumee River during the two-month period (Table 1). At any one site, pH and temperature showed less than 1 pH unit and 6°C variation, respectively, during the two-month period. Both temperature and pH tend to favor precipitation of secondary calcite in the Maumee River rather than its tributaries, whereas the concentrations of calcium, bicarbonate, and carbonate favor precipitation in the tributaries rather than the Maumee River proper.

Calculated Calcite Equilibria

Calcite equilibria in selected stream discharges representing high and low calcium and bicarbonate concentrations found during this study were calculated using the procedure outlined by Garrels and Christ (1965). Ionic strengths (I) were computed from electrical conductivity using the method of Ponnamperuma *et al*. (1966). Concentrations of Ca^{+2} and HCO_3^- were converted to activities by using activity coefficients obtained from Figures 2.15 and 4.5 in Garrels and Christ (1965), which relate activity coefficients to ionic strength. The equilibrium concentration of Ca^{+2}, at standard temperature and pressure, was calculated using measured bicarbonate concentrations and pH. First the activity of CO_3^{-2} was ascertained by substituting the activities of H^+ and HCO_3^- into the following equation and solving for $a_{CO_3^{-2}}$:

$$\frac{(a_{H^+})(a_{CO_3^{-2}})}{(a_{HCO_3^-})} = K_{HCO_3} = 10^{-10.3} \tag{1}$$

The equilibrium concentration of Ca^{+2} was then calculated by substituting $a_{CO_3^{-2}}$ into the following equation and solving for $a_{Ca^{+2}}$ which is converted to concentration:

$$\frac{(a_{Ca^{+2}})(a_{CO_3^{-2}})}{CaCO_{3(s)}} = K_{CaCO_3} = 10^{-8.3} \tag{2}$$

The calculated equilibrium values of Ca^{+2} concentrations are reported in Table 2. In all cases, the calculated equilibrium Ca^{+2} concentrations are considerably less than measured calcium concentrations, implying that measured Ca concentrations are not in equilibrium with the pH and bicarbonate concentrations found in the Maumee River system.

Some of the difference between measured and calculated equilibrium Ca^{+2} concentrations may be due to the formation of ion-pairs involving Ca^{+2}. Analytical determinations of calcium concentrations will not only measure Ca^{+2} ions but also all Ca ion-pair species; thus these ion-pair species must be subtracted from measured calcium concentrations to yield actual Ca^{+2} ionic concentrations (Adams, 1971). The concentrations of $CaHCO_3^+$, $CaCO^o{}_3$, $CaHPO^o{}_4$, and $CaOH^+$ ion-pairs were calculated using equlibrium constants reported by Adams (1971) and measured Ca concentrations. The latter results in the calculation of maximum concentrations for each ion-pair since some of the measured Ca is associated with other ion-pairs, which reduces its activity accordingly. To calculate actual concentrations of all the ion-pairs, all the related

TABLE 2. CONCENTRATIONS OF Ca^{+2}, HCO_3^-, CO_2^{-2}, AND SEVERAL ION PAIRS (CALCULATED AND MEASURED) FOR SELECTED, REPRESENTATIVE SAMPLING SITES IN THE MAUMEE RIVER BASIN

Site and Sampling Date	Measured Stream Water Parameters						Calculated Equilibrium Concentrations							Contribution of ion-pairs to $Ca_m - Ca_{cal.}$ ¶¶ %
		Ca		HCO_3						ion-pairs§				
	pH	mg/l	pCa	mg/l	$pHCO_3$	I*	pCa**	P_{CO_2} †	P_{CO_2} ††	$pCaHCO_3^+$	$pCaCO_3^0$ §§	$pCaHPO_4^0$ ¶	$pCaOH^+$	
Auglaize R. 8/11/76	8.7	70	2.76	149	2.61	0.013	3.83	0.00032	0.00378	4.37	4.23	5.64	6.89	6.5
Maumee R. at S.R.-127 9/8/76	9.1	32	3.10	141	2.64	0.008	4.27	0.00012	0.00185	4.67	4.08	5.93	6.78	14.4
Tiffin R. 8/11/76	8.0	72	2.74	165	2.57	0.010	3.20	0.00179	0.00522	4.28	4.82	5.60	7.55	6.0
Tiffin R. 8/31/76	8.0	75	2.73	286	2.33	0.011	3.43	0.00308	0.01542	4.04	4.59	5.60	7.55	8.0
Maumee R. at S.R.-127 8/11/76	8.9	63	2.80	164	2.57	0.009	4.12	0.00023	0.00476	4.32	3.95	5.65	6.70	10.7
Maumee R. at S.R.-127 8/31/76	9.1	40	3.00	151	2.61	0.009	4.28	0.00013	0.00250	4.56	3.99	5.85	6.70	13.8
Maumee R. at Defiance 8/11/76	8.9	68	2.77	134	2.66	0.009	4.03	0.00019	0.00337	4.38	4.01	5.62	6.67	9.2

* Ionic strength (I) calculated from measurements of electrical conductivity (Ponnamperuma et al., 1966).

** Calculated using measured values for pH and HCO_3 concentrations.

† Calculated using measured values for pH and HCO_3 concentrations.

†† Calculated using measured values for Ca and HCO_3 concentrations.

§ Calculated using equilibrium constants reported by Adams (1971).

§§ Carbonate concentrations were estimated by using measured values for pH and HCO_3 and the equilibrium constant, K_{HCO_3}.

¶ HPO_4^{-2} was taken to be 0.4 mg/l which is the median reported by Jones et al. (1977) for the Maumee River.

¶¶ The concentrations of all four ion pairs were summed and expressed as a percentage of difference between the measured and calculated Ca concentrations.

equations must be solved simultaneously; however, since our only interest was in maximum concentrations of ion-pairs, such a rigorous mathematical solution was not necessary. The calculated maximum concentrations of the selected ion-pairs are reported in Table 2. The concentrations of all four ion-pairs are low (10^{-4} to 10^{-7} moles/l), which agrees with the contention of Garrels and Christ (1965) that the effect of ion-pairs in natural waters less concentrated than sea water is relatively slight. The contribution of ion-pairs to the difference between measured and calculated equilibrium Ca^{+2} concentrations is also reported in Table 2. Note that, in all cases, ion-pairs account for less than 15% of the difference. Thus the formation of ion-pairs can not account for the apparent oversaturation of the fluvial media with calcium.

The partial pressure of CO_2 in the streams which, is required for equilibrium with the measured pH and bicarbonate concentrations, was calculated using the following two equations:

$$\frac{(a_{H^+})(a_{HCO_3^-})}{(a_{H_2CO_3})} = K_{H_2CO_3} = 10^{-6.4} \qquad (3)$$

$$\frac{(a_{H_2CO_3})}{P_{CO_2}} = K_{CO_2} = 10^{-1.47} \qquad (4)$$

The concentrations and activity coefficients of HCO_3^- and H^+ were substituted into Equation 3 which, was then solved for the activity of H_2CO_3. That value was then placed into Equation 4, which was solved for P_{CO_2}. The values obtained for the partial pressure of CO_2 in the streams (Table 2) approximate atmospheric CO_2 partial pressure except for the two Tiffin River samples, which exhibit values which are an order of magnitude higher than atmospheric. Due to respiration of aquatic organisms, decomposition of organic components in the water, and a relatively slow CO_2 exchange process between the river and the atmosphere, the CO_2 content of the river water should be greater than in the atmosphere. Atmospheric CO_2 exchange with the river is particularly slow in sluggish streams characteristic of the Maumee River Basin. If the H^+ ion concentration is a function of dissolved CO_2 content and the CO_2 content is higher than atmospheric, then the pH of the river should be considerably lower than that reported in Table 2. This implies that the pH of the stream is more closely related to ion exchange and additions of strong bases than to the H_2CO_3 content of the stream. Increasing pH's on moving downstream exhibited by data in Table 2 and by Jones et al (1977) tend to substantiate this hypothesis, since the quantity of industrial and municipal wastes and effluent increases on moving downstream.

Consequently, the partial pressure of CO_2 in the river at the selected sites was also calculated, assuming that calcite is in equilibrium with H_2CO_3 (dissolved CO_2) in the river rather than with pH using the following equation:

$$\frac{(a_{Ca^{+2}})(a_{HCO_3^-})^2}{(a_{H_2CO_3})} = 10^{-4.4} \qquad (5)$$

Equation 5 was solved for the activity of H_2CO_3, which was then substituted into Equation 4, which was solved for P_{CO_2}. The CO_2 partial pressures in equilibrium with Ca^{+2} and HCO_3^- are much higher than atmospheric (Table 2), ranging up to 1.5%, but are believed to be quite reasonable for the Maumee River system. Thus the Ca-HCO_3-H_2CO_3-CO_2 system may be more nearly at equilibrium than the H-HCO_3-H_2CO_3-CO_2 system. This would also explain why calcite is not continually being precipitated in the Maumee River system. In either case, it is apparent that the calcium concentrations are not in equilibrium with the pH exhibited by the streams.

Occurrence of Secondary Calcite

X-ray diffraction analyses of all suspended sediments collected in this study were conducted to give a qualitative indication of the presence of secondary calcite. Ratios of calcite to dolomite peaks were used to distinguish between primary and secondary calcite. Calcareous glacial deposits in the lake basin exhibit calcite/dolomite ratios of approximately 1.8 (Smith and Wilding, 1972); thus primary carbonates produce calcite and dolomite peaks of approximately equal intensity as illustrated by the sample from the Auglaize River in Figure 2. Since dolomite is less soluble than calcite and the precipitation of dolomite in fresh water has never been reported, a ratio of calcite-to-dolomite of greater than 1:8 is indicative of secondary precipitation of calcite in the stream, as illustrated by the two Maumee River sites in Figure 1. In the study by Wall and Wilding (1976), the presence of secondary calcite produced calcite peaks 10-15 times the intensity of dolomite peaks. Only one suspended-sediment sample was void of crystalline calcite and dolomite (a sample from St. Rd. 127-Maumee River collected on March 10, 1976) throughout the sampling period. This indicates small amounts of crystalline calcite and dolomite are a basic ingredient of the suspended sediments. Erosion of stream banks (which contain calcareous glacial till and lacustrine deposits) contributes primary calcite and dolomite. A sample from St. Rd. 127-Maumee River collected on April 13, 1976 contained the first evidence of secondary calcite found in this study. The calcite peak was more distinct and 10 times greater in intensity than the dolomite and calcite peaks recorded from earlier samples. During the study period only suspended-sediment samples from the Maumee River at St. Rd. 127, Independence, and Defiance produced high-intensity calcite peaks; however, intermediate calcite peaks (2-3 times the dolomite peak) were observed for samples collected from the Tiffin River and Tiffin River tributary (Figure 1).

In the Maumee River, the occurrence and quantity of secondary calcite were variable, depending on sampling location and date. Figure 2 gives Ca^{+2} concentration and corresponding secondary calcite content (estimated by X-ray analysis) for each sample during the summer months (June-September, 1976). Several observations are evident: (1) The St. Rd. 127-Maumee River site was the most consistent in exhibiting secondary calcite. Except for the sample collected on July 1, 1976, which was collected immediately following a heavy precipitation event, medium to high amounts of secondary calcite were observed throughout the summer. (2) The Defiance-Maumee River site, downstream from St. Rd. 127 approximately ten miles, was next most consistent in exhibiting secondary calcite. (3) The Independence-Maumee River site, five

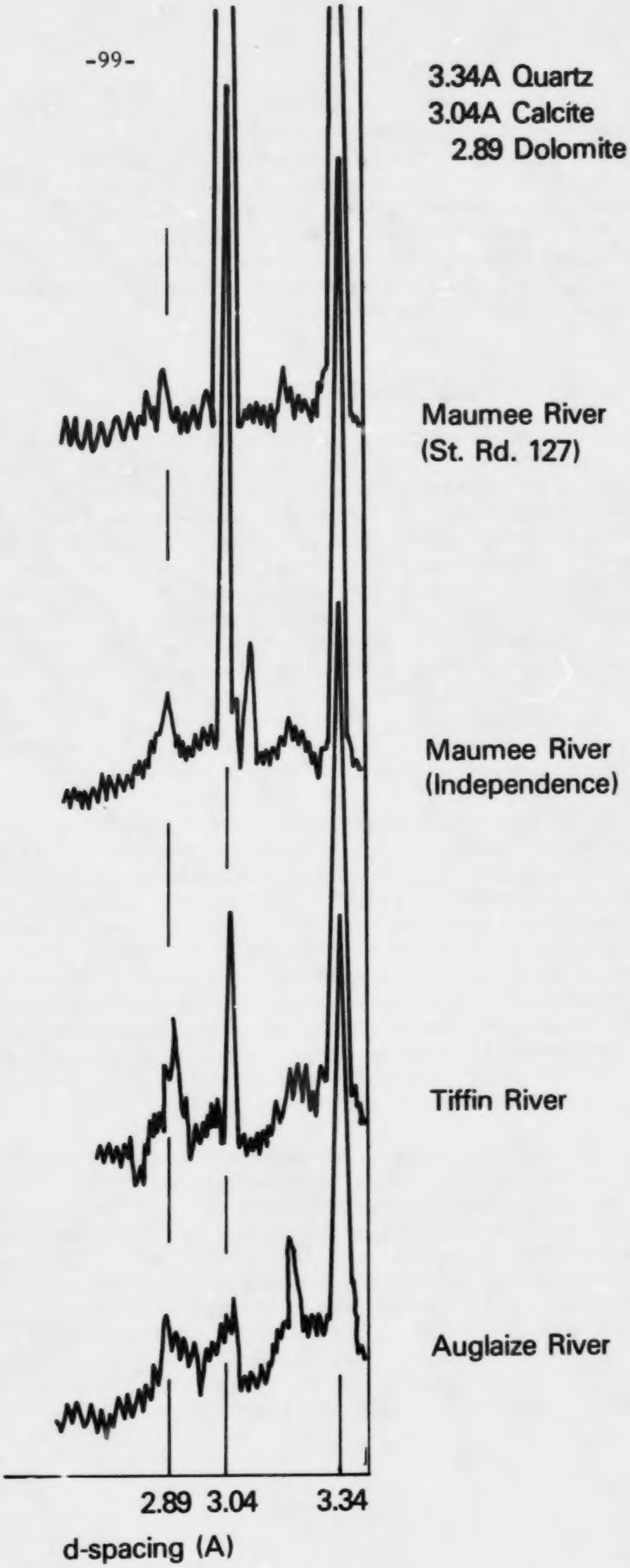

Figure 1. X-ray diffractograms of stream-suspended sediments

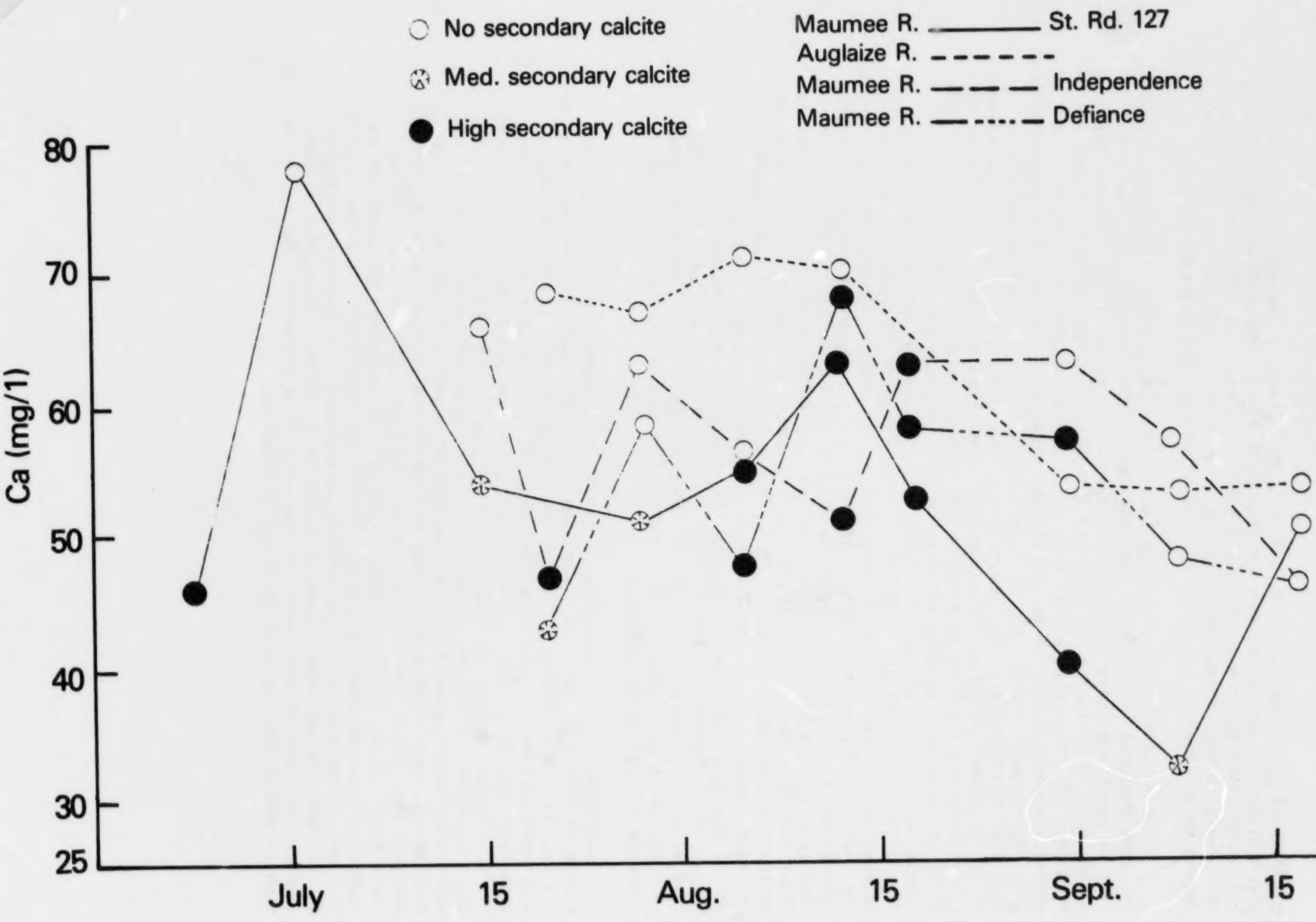

Figure 2. Calcium levels in the stream and occurrence of secondary calcite.

miles downstream from Defiance, was most variable in secondary calcite content. The addition of industrial and municipal wastewater from Defiance and dilution by the Auglaize River may change the solution parameters enough to influence the precipitation of secondary calcite at this site. (4) The Auglaize River showed no evidence of secondary calcite throughout the sampling period.

After April 13, 1976, when high intensity calcite peaks were first observed by X-ray analysis, microscopic observations of the suspended sediment were made to examine primary and secondary calcite crystals and to describe their morphology. Differentiating criteria for distinguishing between primary and secondary calcite crystals were made by observing samples with and without abundant secondary calcite as revealed by X-ray analysis, and noticing morphological differences between the two types of crystals. Secondary calcite crystals were distinctly different than primary calcite crystals in two aspects. First, secondary calcite crystals ranged from 2-20 um in size (with the majority of crystals ranging from 2-12 um), whereas primary calcite crystals ranged from 10-35 um (with the majority of crystals between 15-25 um). The latter is consistent with a study of carbonate particle-size distribution in tills of Western Ohio by Smeck et al (1968), which revealed that calcite attains a maximum in the fine silt (2-20 um) fraction. Second, secondary calcite crystals appeared to be irregular clusters of many individual smaller crystals, whereas primary calcite crystals occurred as angular, dense, discrete units. Secondary calcite crystals in suspended sediment collected from St. Rd. 127-Maumee River tended to be smaller than secondary calcite crystals farther downstream at Independence and Defiance, which indicates the possibility that smaller crystals dissolve at the expense of large crystal growth. Large populations of biological cells were apparent on the slides of suspended sediment. A variety of different species of algae and diatoms were noticed especially from samples collected at St. Rd. 127-Maumee River. This observation prompted the hypothesis that algae control the P_{CO_2} in stream water, which in turn controls the carbonate equilibria.

Quantitative determinations of calcite and dolomite contents in the suspended sediments were determined on composited suspended sediment samples (Table 3). The calcium carbonate equivalents of most of the composited suspended sediment samples were less than 15% with calcite/dolomite ratios of less than 1.5, which is in agreement with data reported by Wall and Wilding (1976) for both medium and high-flow conditions in the Maumee River system. Since these values are very similar to the calcium carbonate equivalent and calcite/dolomite ratios of calcareous glacial deposits in the basin, these samples may contain primary carbonates contributed to the streams by bank erosion. However, a composite sample of suspended sediments collected at State Route 127 on the Maumee River from July 20 to August 18 exhibited a higher calcium carbonate equivalent (38.9%) and calcite/dolomite ratio (6.7) than calcareous glacial deposits, which is indicative of calcite enrichment of the sediments by calcite precipitation in the river. Suspended sediment samples collected at this location from July 20 to August 18 also exhibited high intensity calcite peaks by X-ray diffraction.

TABLE 3. CALCIUM CARBONATE EQUIVALENT AND CALCITE/DOLOMITE RATIOS OF COMPOSITE SUSPENDED-SEDIMENT SAMPLES

Site	Date Sampled	Calcite	Dolomite	Ratio Cal/Dol	$CaCO_3$ Equiv.
		%	%		%
Tiffin R. Tributary	2/19 - 4/13	1.4	1.8	0.8	3.4
"	7/1 - 8/31	7.1	5.2	1.4	12.7
Tiffin River	2/19 - 4/13	1.6	2.1	0.8	3.8
"	7/1 - 9/8	6.0	4.3	1.4	10.7
St. Rd. 127-Maumee R.	2/19 - 4/13	3.8	3.2	1.2	7.3
"	7/1 - 7/15	13.3	7.4	1.8	21.3
"	7/20 - 8/18	33.5	5.0	6.7	38.9
Auglaize River	2/19 - 9/8	2.3	2.4	1.0	4.9
Independence-Maumee R.	2/19 - 4/13	1.6	2.5	0.6	4.3

Parameters Controlling the Precipitation of Secondary Calcite

In this study, the precipitation of secondary calcite was only observed in the Maumee River and only during the summer months. In an earlier study in the Maumee River drainage system (Wall and Wilding 1976), the precipitation of secondary calcite was only observed during low flow. High Ca^{+2} concentrations during low-flow periods were considered the controlling factor in the precipitation of calcite. From the data presented in Figure 2, which relates Ca^{+2} concentrations to semi-quantitative estimates of the abundance of secondary calcite, it is evident that there is considerable variation in Ca^{+2} concentrations (20-50 mg/l) during the three-month-period with no discernable relationship between Ca^{+2} concentrations and the occurrence of secondary calcite. In fact, the Auglaize River generally contained higher Ca^{+2} concentrations than the Maumee River,but no precipitation of secondary calcite was observed in the Auglaize River (Figure 2). In the Maumee River, at the time of the highest recorded Ca^{+2} concentration during the summer months (78 mg/l on July 1, 1976), secondary calcite was not found. Furthermore, many of the observations of abundant secondary calcite occurred during periods of low calcium concentrations. Thus it is concluded that Ca is not the primary parameter controlling calcite precipitation, since at even the lowest recorded Ca^{+2} concentrations (30 mg/l), calcite precipitation was observed.

During the summer months, temperature and pH remained relatively constant, while secondary calcite appeared(June 23) and disappeared (July 1) within short time periods. Also, temperature and pH values recorded in the Auglaize and Maumee Rivers were almost equal throughout the summer, but secondary calcite was never observed in the Auglaize River (Table 3). Thus neither temperature nor pH appears to be an important parameter controlling secondary calcite precipitation in these fluvial systems.

Bicarbonate concentrations not only exhibited considerable variation during the year (Table 1) but also showed considerable variation between sampling periods (Figure 3). However, there is not an evident relationship between bicarbonate concentrations and the occurrence of secondary calcite (Figure 3).

As the study progressed, microscopic observations of slides of suspended sediments revealed a relationship between the abundance of algal cells on the slide and the presence of secondary calcite. Consequently, algal populations were measured on a series of sediment samples collected on September 8. Algal populations ranged from 0.62 x 10^5 (Tiffin River) to 11 x 10^5 (St. Rt. 127-Maumee River) cells/ml (Table 4). Samples collected at State Route 127 on the Maumee River contained 2-3 times more algal cells than any other site and was the only site on that date to show significant quantities of secondary calcite. As a result of these observations, it is speculated that during periods of algal bloom, the partial pressure of CO_2 in the river is reduced by photosynthesis to levels which will result in the precipitation

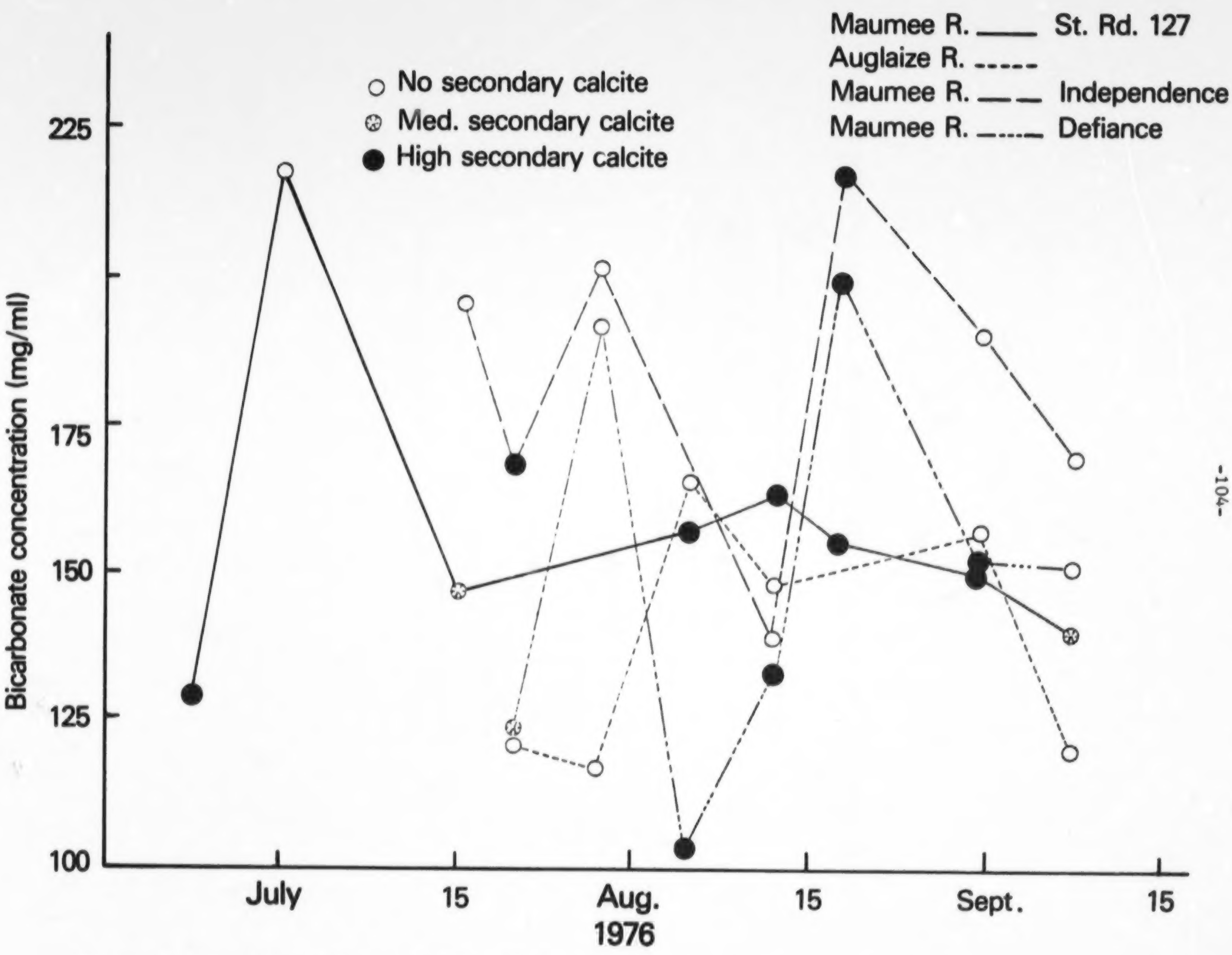

Figure 3. Bicarbonate levels in the stream and occurrence of secondary calcite.

TABLE 4. ALGAL POPULATIONS FROM STREAM SAMPLES COLLECTED ON SEPTEMBER 8, 1976

Stream Site	Algae Population (cells/ml × 10^5)
St. Rd. 127-Maumee River	11.00
Tiffin R. Tributary	2.17
Tiffin River	0.62
Defiance-Maumee River	4.19
Auglaize River	4.34
Independence-Maumee River	2.48

of calcite. As revealed by data in Table 2, the CO_2 partial pressure would not even have to be reduced to atmospheric CO_2 partial pressure to induce calcite precipitation. Additional evidence for this mechanism was observed during late June and early July at St. Rd. 127-Maumee River. Samples collected in late June contained high concentrations of algal cells and secondary calcite; however, samples collected one week later following a heavy rain contained neither algal cells nor secondary calcite. Evidently the increased discharge not only flushed out the system but the increased turbidity of the fluvial media retarded algal photosynthesis. It seems reasonable to expect the CO_2 partial pressure to increase with depth in the stream during algal blooms, due to decreasing utilization by algae. The CO_2 content of the lower part of the stream will be maintained at relatively high levels due to decomposition of organic components and a slow CO_2 equilibration rate. Thus calcite which is precipitated near the surface during algal blooms may redissolve as it settles toward the stream bottom. The hypothesis is supported by examination of the bottom sediments at these sites by Wall et al (1978). By studying the calcium carbonate content and calcite/dolomite ratios, they concluded that calcite had been dissolved from the bottom sediments during the transport process or on the stream bottom. Thus calcite which is precipitated in the stream is not being contributed to the bottom sediments.

3.65 Conclusions

Though secondary calcite is not ubitiquous in the Maumee River drainage system, its occurrence has been established; however, calcite equilibria in the stream system are quite dynamic. Secondary calcite may precipitate and, subsequently, dissolve in relatively short periods of time in the stream and seems to be related to algal blooms. To maintain the relatively high Ca^{2+} concentrations present in the drainage system, CO_2 partial pressure must be considerably higher than atmospheric. Algal blooms reduce the CO_2 content resulting in the precipitation of calcite. Thus it is concluded that CO_2 fluctuation rather than changing Ca^{2+} concentrations is the factor initiating calcite precipitation and dissolution in the Maumee River stream system.

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3.7 Heavy metals in Maumee River Basin water, soil, and sediment

3.71 Abstract

Heavy metal content of streamwater, groundwater, stream-bottom sediments, and soils were measured in the Maumee River Basin. Metal levels were low in all cases and groundwater appears to contribute a significant percentage of the total heavy metal tributary load. Point sources were identified as industrial discharges throughout the Basin but had no detectable effect on downstream water or sediment metal concentrations.

A point-source chromium discharge was monitored above and below Lima, Ohio. Chromium and other metals associated with the point source and other sources in the Lima area were adsorbed by bottom sediment and taken up by rooted macrophytes. This metal assimilation by sediment and aquatic plants could pose a long-term hazard to the local stream environment.

3.72 Introduction

The Maumee River Basin is primarily of agricultural land use with a number of urban centers on tributaries and the Maumee River itself. Heavy metals draining the Basin may be from industrial and municipal point discharges, groundwater, and attached to sediment. Little if any previous information on heavy metals in the Basin is available.

Point sources entering the stream as soluble metal may be diluted by upstream drainage, be adsorbed and retained by stream sediment or be assimilated by stream organisms.

The objectives of this study were:

1. To determine background levels of heavy metals in streamwater, stream sediments, groundwater, and agricultural soils.
2. To determine the fate of a point source discharge of heavy metal to a stream.

3.73 Methods

Metals in water, sediment, soils and bedrock

Stream water and bottom sediments were sampled at 20 locations on four different occasions over a 2½ year period (Figure 1). Sites were chosen along rivers where industrial and municipal effluent was absent or greatly diluted; these sites are listed in Table 1. Samples were taken 10-21-75, 1-20-76, 7-10-76, and 1-29-77. Samples were taken by hand and uniformly across the stream cross-section wherever possible. Water samples and sediment samples (after digestion) were analyzed by flame atomic absorption spectroscopy.

Metals in bottom sediments were digested with 1:1 conc. HNO_3 and conc. HCl. Samples were digested at $\sim 90^\circ$ C for two hours, the digest removed, the samples redigested and the digests combined for analysis. The same procedure was used to determine metal content of surface (0-15 cm) soils from the Defiance County monitored agricultural watersheds and plots at Hoytville (Figure 1, page 4).

In addition, total metals in bedrock samples within the Basin (sampled from a number of quarries throughout the area) were determined, as were dissolved metals in groundwater from 27 wells in Defiance County. These values are intended for comparison only.

Metals from point-source discharge

Lima, Ohio was chosen as the study site to determine the heavy metal variability in the stream environment because the Ottawa River is easily sampled at this point and a well-defined heavy-metal point source (primarily chromium) exists downstream from Lima at the Vistron Corporation. The river at Lima is representative of the stream conditions in most of the Basin, in that it drains both ground moraine and end moraine deposits.

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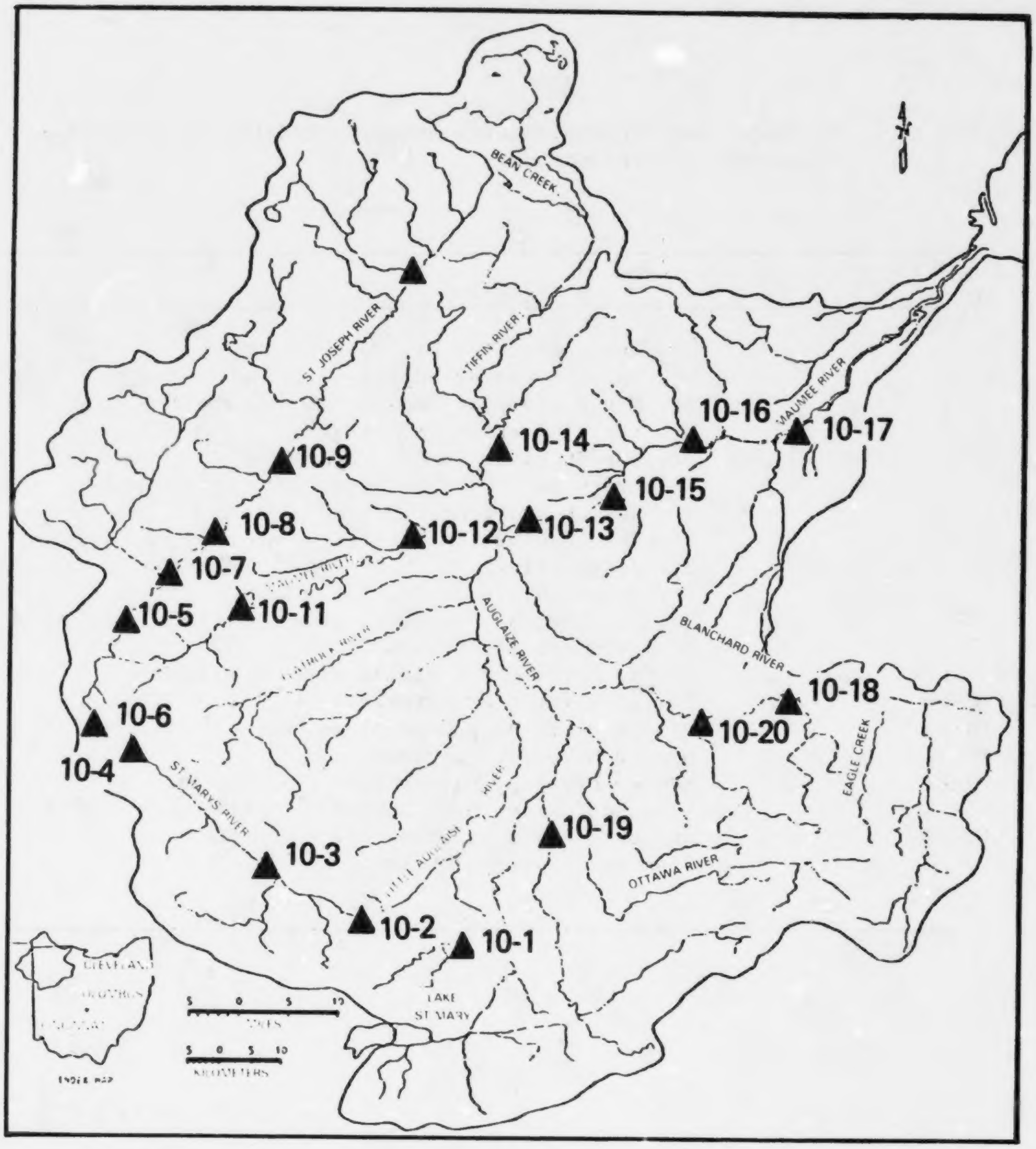

BEAN CREEK
ST JOSEPH RIVER
TIFFIN RIVER
MAUMEE RIVER
10-16
10-17
10-14
10-9
10-15
10-8
10-12
10-13
10-7
10-5
10-11
AUGLAIZE RIVER
BLANCHARD RIVER
10-18
10-6
10-20
10-4
ST MARYS RIVER
EAGLE CREEK
RIVER
10-19
10-3
LITTLE AUGLAIZE
OTTAWA RIVER
10-2
10-1
CLEVELAND
COLUMBUS
CINCINNATI
INDEX MAP
5 0 5 10
MILES
5 0 5 10
KILOMETERS
LAKE
ST MARY

Figure 1. Sampling sites used in determining background concentrations of heavy metals.

Table 1. The locations of sample sites used in studying heavy metal background concentrations.

Sample Number	Sample Site
10-1	St. Marys River at Rt. 33 (U.S.)
10-2	St. Marys River at SR 118
10-3	St. Marys River at Decatur gauging station
10-4	St. Marys River in Ft. Wayne
10-5	St. Joseph River in Ft. Wayne
10-6	Tributary to St. Marys River near Ft. Wayne
10-7	St. Joseph River near Hursh
10-8	St. Joseph River, Newville gauging station SR 249
10-9	St. Joseph River, at U.S. 6 near Edgerton
10-10	St. Joseph River at Rt. 20 (U.S.)
10-11	Maumee River at New Haven gauging station
10-12	Maumee River at Antwerp SR 49
10-13	Maumee River and Auglaize River confluence
10-14	Tiffin River near Evansport
10-15	Maumee River at Independence Dam
10-16	Maumee River at Napolean
10-17	Maumee River at Waterville
10-18	Blanchard River near Dupont
10-19	Auglaize River at Ottoville
10-20	Blanchard River at Ottawa

Sample sites were established on the Ottawa River upstream and downstream from Lima. The upstream site is characterized by low-relief farmland with no industrial discharge. At this point heavy metals could enter only by surface runoff or ground water discharge, i.e. diffuse-source conditions. The downstream site is in an industrial park where waste discharge into the river is common. The river was sampled about 150 feet downstream from one such point source, the Vistron Corporation. At each location 16 water and bottom sediment samples were taken.

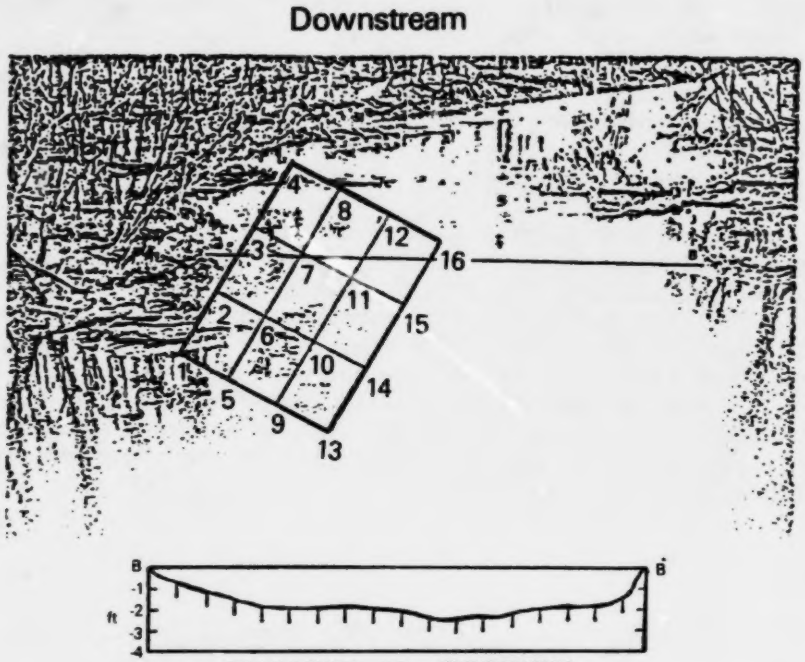
An 18 x 18 feet grid pattern was sampled at each site(Figs. 2 and 3). Water and bottom-sediment samples were collected at the **nodes** numbered 1-16. Nodal numbers increase away from the bank and in the downstream direction with a 6-feet spacing between them.

Water samples were collected about 5 cm below the water surface and stored in polyethylene bottles. Unfiltered water samples were analyzed for Cr, Cd, Pb, Sr, and Zn using a Perkin-Elmer 303 AA spectrophotometer. The precision for this instrument under these conditions is reported in Table 2 in terms of coefficient of variation for duplicate aliquots of water and sediment extracts. The bottom sediment was taken with a piston core sampler. Cores were stored in polyethylene wrapping with only the upper 2 inches being analyzed for metals. The metals were extracted from the sediment with $0.05\underline{N}$ HCL + $0.025\underline{N}$ H_2SO_4 , since the study was concerned mainly with easily extractable metals.

3.74 Results

Dissolved metals in stream and groundwater

Stream water at 20 sampling sites throughout the Maumee Basin was sampled 10-21-75, 1-20-76, 7-10-76 and 1-29-77. Nickel and zinc were detected most frequently and Ni gave the highest concentrations. Strontium was included for comparison. There appeared to be no seasonal effect on heavy metal concentrations,but this is a tentative conclusion considering the low frequency of sampling. No individual site appeared to be higher than others for any of the metals, not surprising since these sites represent diffuse sources only. Mean dissolved metal concentrations are given in Table 3 together with mean values for 27 test wells. Groundwater sources were generally higher than stream water. Based on the analysis of groundwater contribution to total flow, it would appear that groundwater is the major source of dissolved metals in the Maumee. Waterville groundwater accounted for 38% of the total flow in 1976 and,given the concentrations given in Table 3 , the contribution of groundwater to the amounts of each dissolved metal discharged from the Maumee can be estimated (Table 3). The data show that groundwater contributes most of the dissolved metals except **cadmium.**


Downstream
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-1
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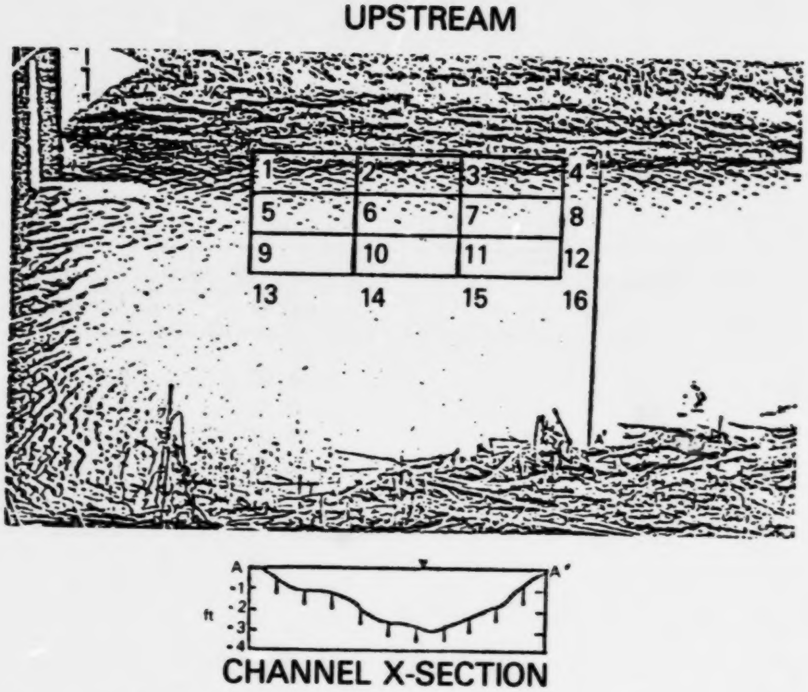
CHANNEL X—SECTION

Figure 2. Sampling grid pattern and channel cross-section of the site of the variability upstream from Lima, Ohio.


UPSTREAM
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12
13
14
15
16
A
A'
-1
-2
ft
-3
-4
CHANNEL X-SECTION

Figure 3. Sampling grid pattern and channel cross-section of the site of the variability downstream from Lima, Ohio.

Table 2. Coefficients of variation (CV) of precision for elemental analysis by AA spectroscopy.

Element	C.V. of Precision (%)	
	water	sediment
Cr	0.02	0.80
Cd	0.01	0.09
Pb	0.04	0.91
Sr	0.06	0.76
Zn	0.10	0.33

Table 3 . Background concentration of heavy metals in the Maumee River Basin and in groundwater (1975-77)

	Streamwater Background (ug/ml)	Groundwater (ug/ml)	Percent of total discharge as groundwater*
Cd	0.011 (20.0)†	0.009	33.4
Co	0.010 (21.3)	0.080	83.1
Cr	0.003 (20.0)	0.098	95.2
Cu	0.003 (16.3)	0.250	98.1
Ni	0.082 (77.5)	0.950	87.7
Pb	0.020 (28.8)	0.094	74.2
Zn	0.021 (85.0)	0.954	96.5
Sr	0.570 (100.0)	1.650	64.0

* Assumes 38% of total discharge in groundwater

† Percent of samples where metal was detected

Heavy metals in watershed soils and Maumee River bottom sediments

Table 4 gives the mean heavy metal concentrations of the surface soil horizons of the Defiance county and Hoytville sites and bottom sediments from the 20 metal sampling sites in the Maumee. Metal content of limestone bedrock of the area is included for comparison. Values given in Table 4 are for aqua regia extraction. This procedure does not extract all the structural metal, i.e. metal held within the crystal lattice of minerals, but it does extract those compounds that would be environmentally active. Of the metals, cadmium has the lowest concentration and zinc the highest in both soil and sediment. Metal concentrations in both soil and sediment appear to reflect bedrock composition somewhat. Only cobalt appears to be enriched in the sediment compared to soil while all other metals are considerably lower in the sediment. Variability was remarkably low and there appeared to be little regional differences. In addition, metal concentrations were not correlated with each other. It should be reemphasized that the sampling sites were chosen to reflect background metal levels and were not close to known point sources. While our estimates of sediment-bound metals is underestimated because our extraction procedure does not extract total metal, the data still show that dissolved metal **accounts** for a high percentage of the total load. Taking into account our findings that the groundwater accounts for a high percentage of the dissolved load, it would appear that metals in groundwater are the major source of metals leaving the Maumee.

Point-source metal discharge

Concentration means and ranges and coefficients of variation were determined for each metal at both locations for water and bottom sediment (Table 5). The high concentrations of all elements except strontium in the downstream water and sediment samples reflect the point-source loading at Lima. The major component of this discharge is chromium, and this is reflected in the values in Table 5. Chromium in excess of 0.4 mg/l persisted

Table 4 .Concentrations of heavy metals in Maumee River Basin soils, bottom sediments , and limestone bedrock.

	Soils			Sediment			Bedrock
	Range	Mean	S.D.	Range	Mean	S.D.	
				μg/g			
Cd	0.10-0.70	0.35	0.26	0.04- 0.39	0.15	0.09	1.94
Co	1.80-2.30	1.98	0.22	4.25-14.31	9.11	2.26	1.27
Cr	12.00-13.80	15.30	4.17	0.72- 2.54	1.55	0.46	2.63
Cu	9.60-27.80	20.20	8.62	4.38-10.11	6.49	1.27	8.52
Ni	25.80-42.00	33.75	6.63	6.42-16.89	11.21	2.39	34.12
Pb	21.60-29.40	25.20	3.23	3.84-10.70	7.33	1.55	33.50
Zn	41.30-69.60	49.15	13.65	6.95-24.68	15.77	3.32	250.50
Sr	—	—	—	50.10-93.60	71.77	7.89	57.80

Table 5. Elemental analysis of 16 grid samples from each site (upstream and downstream water and bottom sediments).

Element	Concentration		C.V.
	Mean	Range	%
	Upstream Water (mg/l)		
Cr	0.12	0.10 - 0.18	4.1
Cd	0.007	0.005 - 0.200	7.0
Pb	0.02	0.01 - 0.02	5.4
Sr	0.782	0.750 - 0.800	6.3
Zn	0.018	0.010 - 0.030	9.1
		Mean	6.4
	Downstream Water (mg/l)		
Cr	3.93	0.10 - 6.98	8.1
Cd	0.060	0.050 - 0.070	1.0
Pb	1.10	1.08 - 1.13	1.5
Sr	0.754	0.640 - 0.820	3.3
Zn	0.912	0.880 - 0.980	1.4
		Mean	3.1
	Upstream Bottom Sediment (ug/g)		
Cr	1.69	1.48 - 2.10	9.3
Cd	0.94	0.52 - 4.38	11.2
Pb	1.1	0.5 - 1.5	6.2
Sr	26.9	17.7 - 29.3	10.6
Zn	1.30	1.09 - 9.38	13.5
		Mean	10.1
	Downstream Bottom Sediment (ug/g)		
Cr	195	176 - 230	51.4
Cd	1.20	0.76 - 12.10	19.6
Pb	19.3	15.6 - 22.6	9.5
Sr	29.7	19.8 - 34.7	31.6
Zn	12.10	17.60 - 26.30	13.5
		Mean	25.1

four miles downstream from the discharge tunnel, hugging the river bank of the source. Under diffuse source conditions, concentration variability in water was much lower in the higher velocity (main flow) portion of the stream than near the bank (Fig. 4). The difference is more than likely a direct result of mixing in the more turbulent stream water. This suggests that sampling under diffuse source conditions should be carried out in the most rapidly flowing part of the stream. Strontium concentration is high throughout the basin since the area is underlain by Silurian and Devonian carbonates containing $SrCO_3$.

The variability in the metal content of the downstream water was due to effluent mixing and dilution. Chromium was the best element to demonstrate mixing (Fig. 5). In grid observation numbers 1-6, the variability was low because the effluent was still highly concentrated. At grid numbers 7-10, mixing occurs and variability was high. Outside of the mixing zone nodes 10-16, both concentrations and variability were low.

In contrast to the easily recognized trend of the water, the bottom sediment at the same nodes had a highly variable chromium concentration (Fig. 6). The coefficient of variation for these data is 51.4 percent. The variation is attributed to shifting of sediment during high flow, and differences in sediment distribution and grain size. The coefficient of variation suggests taking a large number of samples to approach the mean concentration.

In order to compare the data in terms of sample numbers needed to maintain a precision of 10 percent on either side of the mean, limit-of-precision curves (95 percent confidence interval) were constructed for each element and graphed for each location, water sample, and bottom sediment. In Figure 7 such a graph is presented for the upstream bottom sediments. Zinc is the most variable, with lead being the least variable; precision increases as sample number increases. Similar graphs were obtained at the downstream location; however, downstream, chromium was the most variable element as demonstrated by the CV's in Table 5 .

Sample numbers needed to maintain a precision ± 10 percent on either side of the mean were calculated and are presented in Table 6. The number of bottom-sediment samples required were higher than for water samples. Since upstream and downstream values were averaged, chromium required the largest number of samples for ± 10 percent precision. The number of samples which should be taken to meet the specified precision was found to be at least 4 water and 7 bottom sediment at any one location. With a change in variables, such as river stage, groundwater contribution, industrial discharge, etc., the sample number would be subject to change. The variability encountered in stream-sampling programs, especially sediments, necessitates preliminary study to determine the degree of sampling required. Monitoring the distribution of point-source pollutants in stream water and sediments will require a carefully designed monitoring program that considers the dynamics of the pollutant in the water-sediment system as it mixes with the diffuse-source load.

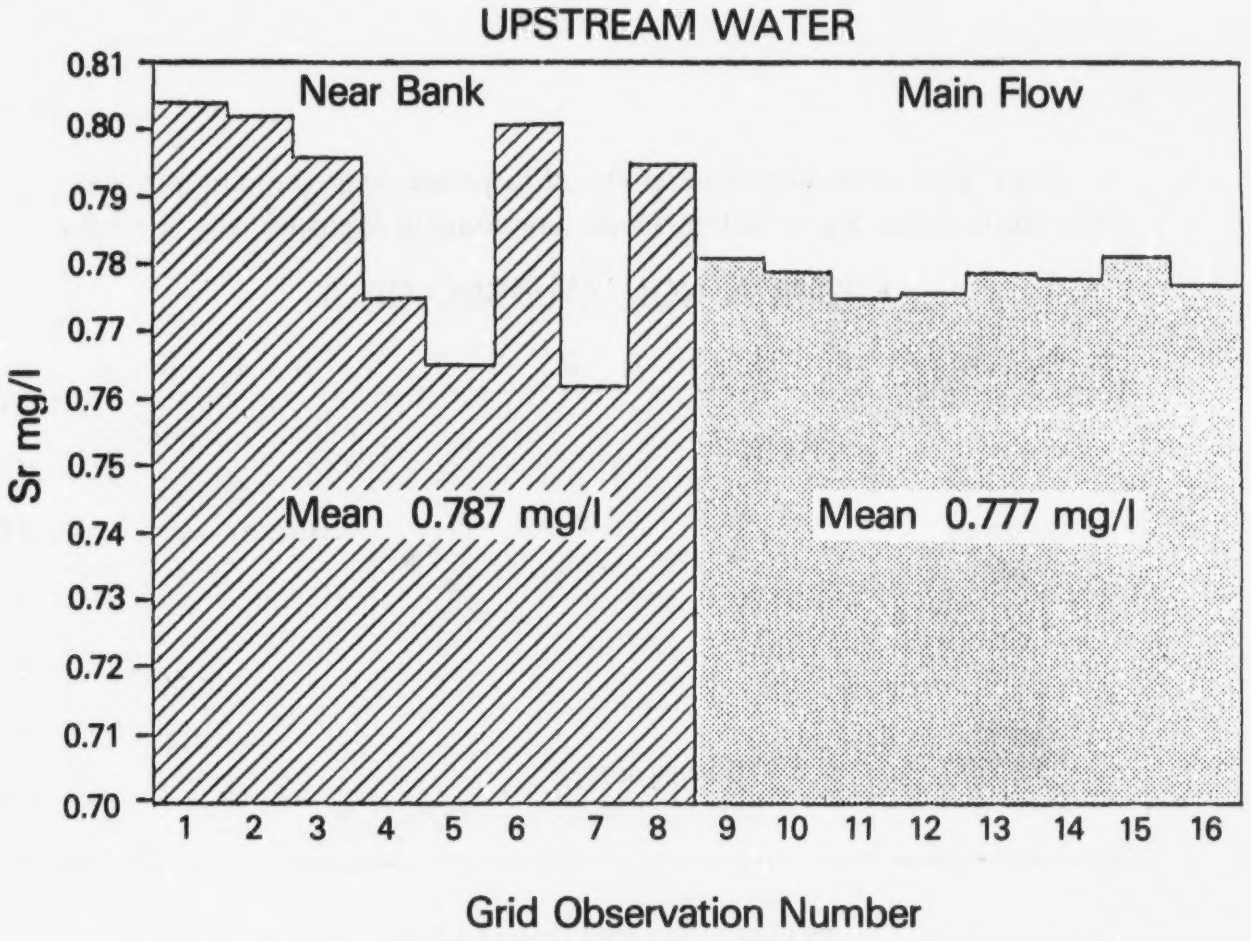
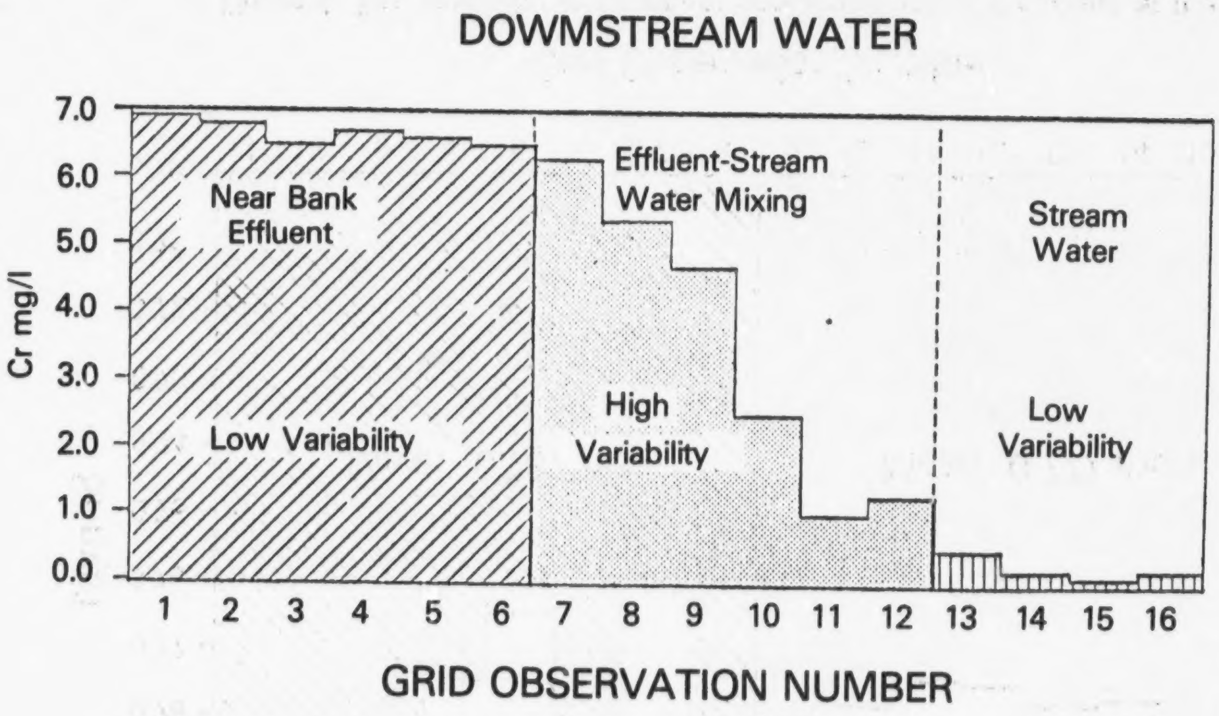


Figure 4. The variability in strontium concentrations in the water at the near-bank and the main-flow sampling points upsteam from Lima, Ohio.



DOWMSTREAM WATER

Figure 5. The variability in chromium concentration in the water at the near-bank and the main-flow sampling points downstream from Lima, Ohio.

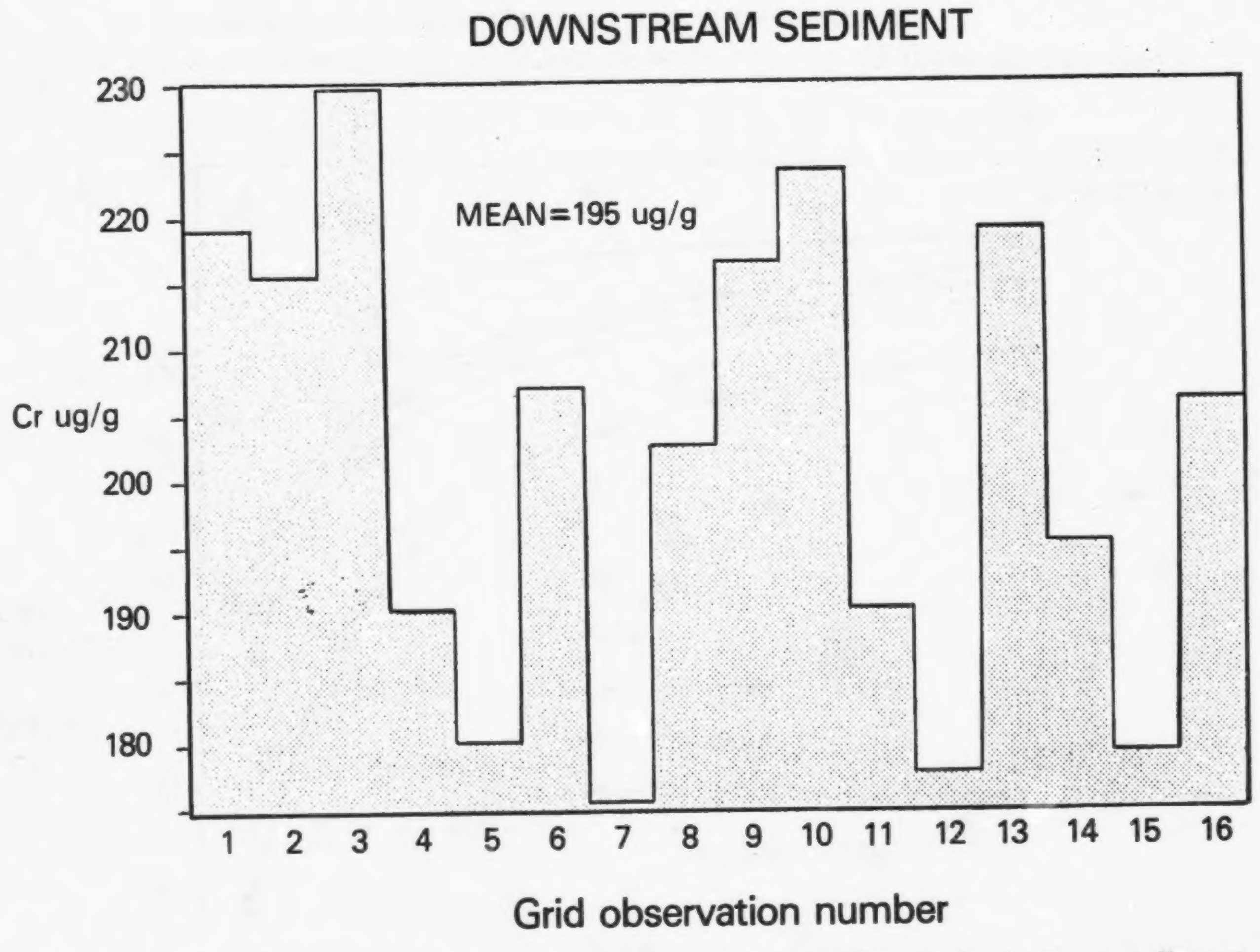


Figure 6. The variability in chromium concentration in the bottom sediment at the sampling location downstream from Lima, Ohio.

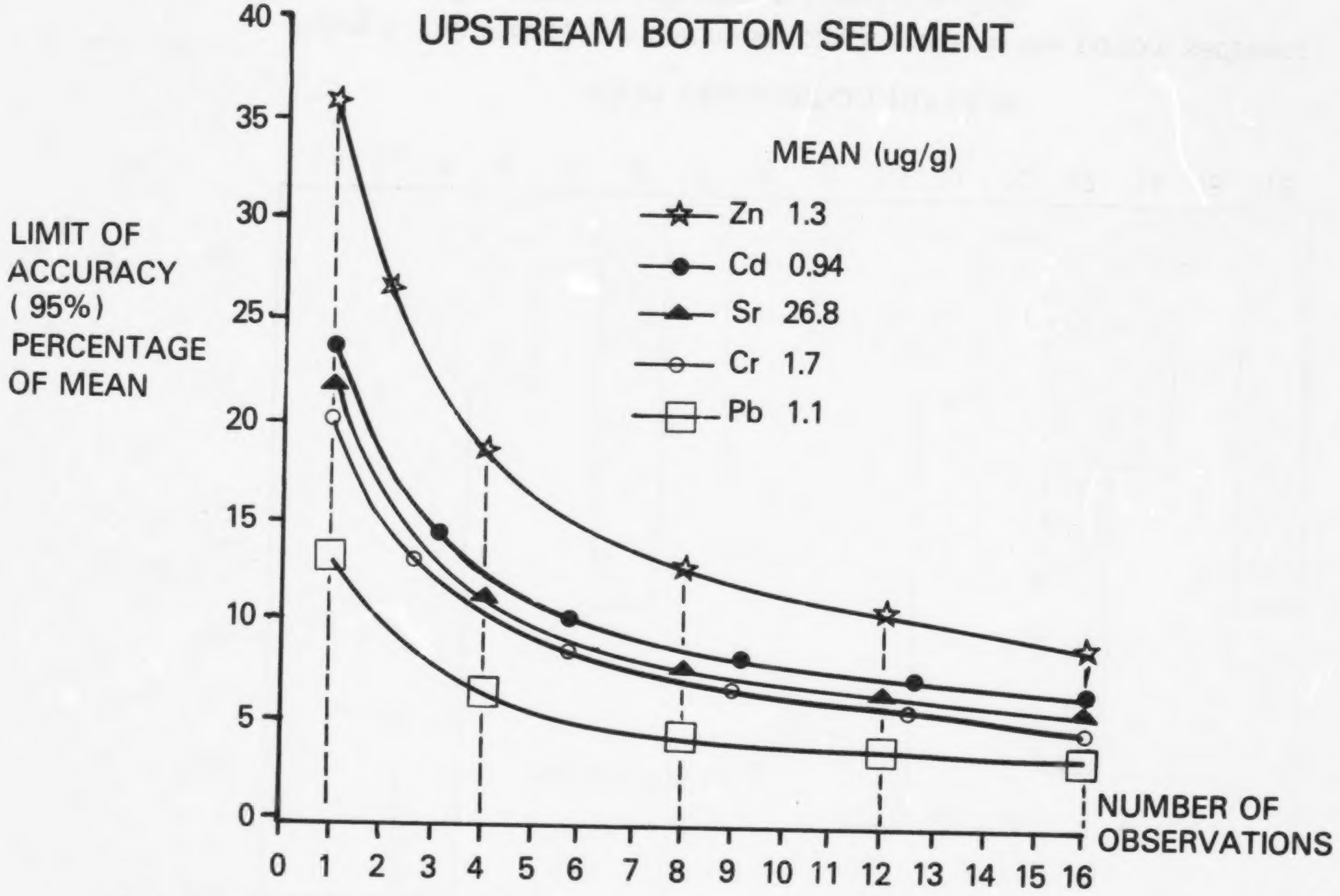


Figure 7. Limit of accuracy (95%) curves as percentage of the mean for elements in the bottom sediments upstream from point source.

Table 6. Sample number required to maintain ±10% precision of the mean concentration of each element.

Element	Water	Sediment
Cr	7	14
Cd	5	6
Pb	2	4
Sr	4	6
Zn	5	5
Mean	4	7

The data indicate: 1) under diffuse-source conditions, heavy metal variability increases laterally away from the main channel flow; 2) in close proximity, approximately 150 feet downstream from point sources, heavy metal variability in bottom sediment is higher than that of the stream water.

Heavy Metals in River Bank Vegetation

Samples of plants, mainly river grasses and weeds, were collected at sites upstream and downstream from Lima. Sixteen samples were collected at each location, once during the growing season and once during the winter. Samples were digested by both the dry-ash method and by perchloric acid digestion. There was no significant difference between the two digestion methods. The arithmetic means of the concentrations are reported in Table 7.

From the vegetation analysis the following conclusions can be made: 1) stream environment vegetation concentrates heavy metals; 2) metal uptake by vegetation is much greater downstream of cities; 3) river grasses release a high proportion of their metal content during the autumn. Stream vegetation, therefore, is one mechanism for concentrating heavy metal on stream bottoms.

Heavy Metal Point Sources

Heavy metals appearing in anomalously high concentrations were found in the vicinity of eight cities (Table 8). It is probable that the high concentrations of various heavy metals in the water and sediment near these eight cities are a result of industrial pollution.

3.75 Conclusions

Levels of heavy metals in Maumee River Basin water, soils,and sediments reflect normal geochemistry of the area and indicate that point source discharges are small compared to loadings from natural sources.

Groundwater appears to contribute a substantial portion of the heavy-metal load from the Basin.

Point-source discharges are adsorbed by sediments in the stream and taken up by rooted macrophytes. These discharges may pose a threat to local downstream biota.

Table 7. Heavy-metal concentrations in living and dead river vegetation along the Ottawa River (ug/g).

Element	Growing Vegetation		Dead Vegetation	
	Upstream Lima	Downstream Lima	Upstream Lima	Downstream Lima
Cd	0.001	0.89	0.001	0.001
Co	1.27	34.2	0.02	1.2
Cr	1.35	440.0	0.02	64.8
Cu	48.72	537.0	1.78	62.6
Ni	9.78	98.5	0.90	5.6
Pb	0.95	6.3	0.02	1.01
Sr	35.7	105.7	10.20	45.7
Zn	2.55	15.9	0.85	9.8

Table 8. Heavy metals detected in high concentrations in stream water and sediments near cities.

City	Sediment	Water
Butler, Ind.	Cd,Co,Cu,Ni,Pb	Cd
Decatur, Ohio	Cr,Cu	Cd
Defiance, Ohio	Cr,Ni,Pb	Pb
Findlay, Ohio	Ni	Co,Sr,Pb
Fort Wayne, Ind.	Cd,Cr	Co
Hudson, Mich.	Cd,Co,Cr,Cu,Ni,Pb, Sr,Zn	Cu
Lima, Ohio	Cr,Cu,Pb	Cr
Maumee, Ohio	Cd,Cr,Cu,Ni,Pb,Zn	Cd

3.8 Pesticides in watershed soils and Maumee River Basin bottom sediments

3.81 Abstract

A pesticide scan was run on surface soils from the monitored agricultural sites in Defiance County and at Hoytville and bottom sediments from the Maumee River and its tributaries. Of the compounds screened, p,p'-DDD was found in one soil and p,p'-DDD, p, O-DDD and dieldrin were detected in bottom sediments from Maumee River tributaries. No other compounds were detected in any samples. Insecticide usage is low on the corn, soybeans, and wheat crops,which account for most of the agricultural production in the Basin.

3.82 Methods and Materials

Surface (0-15 cm) soil samples were taken from each of the monitored watersheds in Defiance County and a composite sample from the plots at Hoytville (Figure 1, page 4). The samples were air-dried, ground and screened and the < 2 mm fraction retained. Bottom-sediment samples were taken by a scuba diver from the 0-10 cm water-sediment interface and sealed in plastic jars. Sediment was oven-dried prior to pesticide analysis. Samples were taken from the Auglaize and Tiffin Rivers and the Maumee River at Independence Dam (Figure 1, page 4). Pesticide analysis was performed at The Ohio State University Pesticide Analytical Laboratory by Dr. Acie Waldron.

Fifty grams of sample was blended with 300 ml of glass distilled acetone in a Waring blender for 5 minutes at slow speed (30 volts on the Variac). The solution was filtered under light vacuum through Whatman #1 filter paper and the volume of filtrate measured.

The volume of filtrate was reduced by evaporation to 150 ml and then combined with 500 ml of 2% sodium sulfate solution in a 1-liter separatory funnel.

The aqueous solution was extracted by shaking vigorously for 1-2 minutes in sequence with 200 ml and 100 ml of glass distilled **petroleum ether.** The combined petroleum ether extracts were backwashed by shaking with 500 ml of 2% $NaHCO_3$. The volume of petroleum ether extract was recorded, then reduced by vacuum rotary evaporation to approximately 20 ml volume.

The concentrated extract was placed on a column of cleanup material in a 250 ml reservoired, 19 mm diameter chromatography column containing from bottom to top a glass wool plug, 2½ inches of activated florisil, 2½ inches of silica gel, and topped with 1 inch of anhydrous sodium sulfate.

The pesticide residues were eluted from the column in sequence with 200 ml of 5% benzene in petroleum ether, 250 ml of 100% benzene, and 200 ml of 10% ethyl acetate in benzene. Organochlorine pesticides elute in the first two eluates and organophosphate pesticides in the ethyl acetate-benzene eluant.

Eluates were then reduced to an appropriate volume with a rotating flask vacuum evaporator and aliquots injected on the columns of a gas chromatograph (Tracor 222 equiped with multiple detectors).

Organochlorine pesticide residues were determined in response to an Electron Capture detector with additional detection and confirmation by a Hall Electroconductivity detector. Organophosphate pesticide residues were determined by response to a Flame Photometric detector specific for phosphorus detection.

3.83 Results

The results of the pesticide scan for watershed soils and Maumee River Basin bottom sediments are given in Table 1. Pesticide standards used in the scan are given below:

Organochlorine
- Standard A - Aldrin; o,p-DDE; o,p-DDD; p,p'-DDD
- Standard B - Heptachlor; p,p-DDE; o,p-DDT; p,p'-DDT
- Standard C - Lindane; Heptachlor epoxide; Dieldrin; Methoxychlor

- Chlordane
- Toxaphene

Organophosphate
- Thimet (Phorate)
- Diazinon
- Malathion
- Methyl Parathion
- Ethyl Parathion
- Guthion (will not respond without forming a derivative)

Each extract solution was analyzed with all three dectectors, although the identity of peaks on the chromatogram correspond only to the type of eluate and the detector system which has been determined in past research to relate to the specific pesticide.

Several peaks were observed on the chromatogram that were not identified. Extraneous peaks are common with the Electron Capture detector. Some very prominent peaks were detected with the Electron Capture detector or the Hall Electroconductivity detector or with both detectors but were not identified. The Electron Capture detector responds to any compounds that will capture electrons (chlorinated hydrocarbons more pronounced and sensitive), and the Electroconductivity detector is specific for chlorinated compounds but not restricted to pesticides.

Table 1. Pesticide Residues Found in Soil and Sediment Samples.

Sample No.	Sample Description	Pesticide Residues (ppb) Organochlorine	Organophosphate
	Watershed Surface Soils	1/	1/
1.	Hoytville	None	None
2.	Hammersmith Roselms	None	None
3.	Hammersmith Broughton	None	None
4.	Speiser Paulding	None	None
5.	Rohrs Lenawee	0.89 p,p'-DDD	None
6.	Heisler Blount	None	None
7.	Crites Roselms	None	None

Table 1. (Cont)

Sample No.	Sample Description	Pesticide Residues (ppb) Organochlorine	Organophosphate
	Bottom Sediments		
8.	Maumee River (Independence Dam)	None	None
9.	Auglaize River	2.77 p,p'-DDD	None
10.	Tiffin River	0.94 Dieldrin	None

1/ None means no residues detected at the sensitivity of the method which could be identified in relation to the pesticide standards used.

A very prominent peak was chromatographed in the 10% ethyl acetate-benzene eluate of the ten samples,but it did not correspond to any of the standards used. The retention time did not basically correspond to that of other organophosphate standards analyzed in previous research in the laboratory including DDVP, Ronnel, Ciodrin, and Dyfonate. Dimethoate also required the formation of a derivative for gas chromatographic detection. In addition, one or two prominent peaks were observed in the chromatograms of the 5% benzene in petroleum ether eluate and the 100% benzene eluate. These peaks did not correspond to any of the standards; in addition, under the conditions of the research procedures, the organophosphate pesticides related to the standards used should have eluted only in the ethyl acetate-benzene solution. Sample No. 10 had a very prominent peak with the retention time for diazanon, but it was in 100% benzene eluate and no indication of detection at all in the ethyl acetate-benzene eluate. The Flame Photometric detector is specific for phosphorus compounds but is not limited to only the organophosphate pesticides. Thus the peaks observed are likely due to a phosphate or phoshorylated compound, but the identity remains unresolved at present.

Based on the results of this scan, no further analyses were made. Waldron (1974) in a previous study on the Maumee and several other Ohio tributaries draining into Lake Erie found similar low values for water and bottom sediments. When detected at all, pesticide residues were generally less than 10 ppb, while triazine herbicides were usually less than 50 ppb. He found that DDT, diazanon and dieldrin were the common insecticides detected, while atrazine was the herbicide found most frequently. The generally low levels of insecticides found in the Maumee reflect the land use of the area. About 70% of the Maumee Basin is in cropland and,of that, grain crops are dominant. Insecticide usage by grain farmers in Ohio is quite low, although it is expected that there will be some increase in insecticide application as acreages of minimum and no-till increase. Herbicide usage is more common with atrazine the most common material. It is recommended at rates of 1-4 kg/ha for corn (Ohio Agronomy Guide, 1978), while materials such as lasso (1-3 kg/ha) plus lorox or sencor (0.5 to 2 kg/ha) are recommended for soybeans. Herbicide usage on wheat is minimal. Herbicide usage by Ohio grain farmers continues to increase as more and better compounds are introduced and will be an integral part of minimum or no-till farming in the future. Most pesticides are applied at or near planting and so discharge to streams should be greatest in late April through May in the Maumee. Therefore, pesticide runoff should only be significant in the early spring thaw events as residues from the previous year's application. This will not be a problem with the more degradable compounds.

3.84 Literature Cited

1. Agronomy Guide. 1978-1978. Bulletin 472. Cooperative Extension Service, The Ohio State University.

2. Waldron, A.C. 1974. Pesticide Movement from Cropland to Lake Erie. EPA Tech. Series. EPA 660/2-74-032.